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③ オレフィンの重合方法

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明 細 書

1. 発明の名称

オレフィンの重合方法

2. 特許請求の範囲

- (1) (A) マグネシウム化合物(II)の炭化水素溶液と炭状のタタニ化合物(III)を接触させて固体生成物を形成させるか、或はマグネシウム化合物(II)とタタニ化合物(III)との炭化水素溶液を形成した後、固体生成物を形成させ、
- この際、固体生成物の形成を、モノカルボン酸エステル、脂肪族カルボン酸、脂肪族水素、タタニ、脂肪族エーテル、脂肪族カーボネート、アルコキシ基含有アルコール、アリールオキシ基含有アルコール、 β - α - α - α 結合を有する有機チエチ化合物及び β - α - α - α 結合を有する有機リン化合物より成る群から選ばれた少なくとも一種の電子供与基(B)の存在下に行い、且つ固体生成物の形成時もしくは形成後に、固体生成物に多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルを溶解させることにより得られるマグネシウム、タタニ、ハロゲン及び多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルを必要成分としてなる固体タタニ触媒成分、
- (B) 周知触媒成分、或は新しい触媒成分の有機金属化合物触媒成分、及び
- (C) β - α - α - α 又は β - α - α - α 結合を有する有機チエチ化合物触媒成分
- から形成される触媒系の存在下に、オレフィンを重合もしくは共重合させることを特徴とするオレフィン重合体もしくは共重合体の製造方法。

3. 発明の詳細な説明

発明は、オレフィンの重合(以下、オレフィンの重合)をも包含して用いることがあ

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る)によつて、オレフィン重合体(以下、オレフィン重合体)を製造して用いることがある)を製造する方面に関する。とくには、炭素数3以上の α -オレフィンの場合に適用した場合、高立 体異性重合体を高収率で得ることのできるオレフィン重合体の製造方法に関する。さらには、炭素数3以上の α -オレフィンの場合において、重合に際して水素等の分子量調節剤を用いて重合体のモルティンダツタスを定めても、重合体の立体異性性の低下が少ないオレフィン重合が可能なる方法に関する。また、本発明においてスラリー重合や気相重合を併用した場合に、流動性良好でしかも組成分布の優れた重合体又は単状重合体の製造が可能で、更に高比量も優れたオレフィンの重合方法に関する。また重合時間の経過に伴う活性低下が極めて少ない利点も有するオレフィンの重合方法に関する。

更に詳しくは、本発明は

- (A) マグネシウム化合物(II)の炭化水素溶液と炭化のタタン化合物(III)を重合させて固体生成物

重合化合物組成成分、及び

- (C) β - α -C又は β - α -H-C結合を有する有機タイ置化合物組成成分

から形成される組成成分の存在下に、オレフィンを重合もしくは共重合させることを特徴とするオレフィン重合体もしくは共重合体の製造方法に関する。

マグネシウム、タタン、ハロゲンおよび電子供与体を必要成分とする固体組成成分の製造方法についてはすでに多くの提案があり、該固体組成成分を炭素数3以上の α -オレフィンの場合に利用するとき、高立 体異性重合体を高い収率で得ることが可能であることも知られている。しかしながらその多くは、さらに活性や重合体の立 体異性性などにおいて一層の改良が望まれている。

例えば重合体の後処理操作を簡便にする高品質のオレフィン重合体を得るためには、立 体異性重合体の組成成分が非常に高く、しかも重合体組成成分の重合 収 率が非常に大きくなくてはならない。従来技術の設備は、該例とする重合体 組

を形成させるか、或は

マグネシウム化合物 (II)とイタン化合物(III)との炭化水素溶液を形成した後、固体生成物を形成させ、この際、固体生成物の形成を、 α -ノルボルネン系エステル、脂肪族カルボン酸、脂肪族水素、タタン、脂肪族エーテル、脂肪族カーボネート、アルコール基含有アルコール、アリールオキシ基含有アルコール、 β - α -C結合を有する有機タイ置化合物及び β - α -H-C結合を有する有機リン化合物より成る群から選ばれた少なくとも一種の電子供与体 (D)の共存下に行い、且つ該固体生成物の形成時もしくは形成後に、該固体生成物に多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルを添加させることにより得られるマグネシウム、タタン、ハロゲン及び多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルを必要成分としてなる固体タタン組成成分、

- (D) 同族元素類(炭素以外の第IV族元素)の有機化合物

物によつては、上記組成成分において可成の水率にあると見えるものもあるが、成形時の長短に係わる重合体中の残存ハロゲン含有量の点から見れば、十分な性能を有していると見えるものは数少ない。しかもその多くは、モルティンダツタスの大きい重合体を製造するときには、収率や立 体異性性などの少なからざる低下をひき起こすという欠点を有している。

同一出願人は、特開昭54-8111号公報において、炭素数3以上の α -オレフィンの重合にとくに際し、該固 体組成成分が均一で、流動性の良好なオレフィン重合体もしくは共重合体の製造について提案した。この提案においては、その固体タタン組成成分の形成に際して、利用する電子供与体として多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルの使用については全く言及されていない。更に、これらエステルと前記電子供与体(D)との併用に関しても、また更に、これらと前記(C)に特定される有機タイ置化合物組成成分 併用に関しても、何 言及されていない。

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本発明は、一層改良されたオレフィンの重合方法を提案すべく研究を行つてきた。

その結果、前記オレフィン組成成分(A)に特選された電子供与体(B)と多価カルボン酸エステル及び/又は多価ヒドロキシ化合物エステルの併用系のオレフィン組成成分と、前記(B)及び(C)から形成される新しいタイプの触媒を用いることによつて、収率、収率分率、分子形状、分子量などの優れた重合体が形成でき、しかも、このような優れた重合体が高い触媒活性をもつて、且つ又、重合時間の経過に伴う活性低下が極めて少ないという利点を伴つて得られることを発見した。

更に又、重合に際して、分子量調節剤とえば水素を重合系に共存させてマルチインデックスの大きい重合体を得ようとする、立構異性性が少なからず低下するという従来法における欠陥も低減され、又、少量の水素の利用でマルチインデックスの調節が可能となる利点に加えて、水素の初め分子量調節剤の利用によつて、むしろ触媒活性が向上するという予想外の利点も得られることが

マグネシウム、2-エステル-キソキシマグネシウムの様なアリロキシマグネシウム；フェノキシマグネシウム、ジメチルフェノキシマグネシウムの様なアリロキシマグネシウム；ラウリン酸マグネシウム、ステアリン酸マグネシウムの様なマグネシウムのカルボン酸塩などを例示することができる。また、該マグネシウム化合物は他の金属との錯化合物、錯化合物あるいは他の金属化合物との混合物であつてもよい。さらにこれらの化合物の2種以上の混合物であつてもよい。これらの中でとくに好ましいマグネシウム化合物は、ハロゲン含有マグネシウム化合物、とりわけ塩化マグネシウム、アルコキシ塩化マグネシウム、アリロキシ塩化マグネシウムである。

マグネシウム化合物の炭化水素溶液を形成するのに使用する炭化水素溶液としては、ベンゼン、ヘキサン、ヘプタン、オクタン、デカン、ドデカン、テトラデカン、灯油などの脂肪族炭化水素；シクロペンタン、メチルシクロペンタン、シクロヘキサン、メチルシクロヘキサン、シクロオク

タン、シクロヘキセンの様な脂環族炭化水素；ベンゼン、トルエン、キシレン、エチルベンゼン、タリエン、シメンの様な芳香族炭化水素；ジクロルエタン、ジクロルプロパン、トリクロルエチレン、四塩化炭素、シクロペンゼンの様なハロゲン化炭化水素などを例示することができる。

炭化水素溶液に溶解したマグネシウム化合物を得るには、それらの化合物及び溶媒の温度によつても異なるが、通常を単に混合する方法、混合して加熱する方法、該マグネシウム化合物可溶性の電子供与体、たとえば、アルコール、アルデヒド、アミン、カルボン酸、エーテル、それらの任意の混合物、更にはこれらと他の電子供与体との混合物などを共存させ、必要に応じて加熱する方法などを採用することができる。

例えば、ハロゲン含有マグネシウム化合物をアルコールを用いて炭化水素溶液に溶解させる場合について述べると、炭化水素溶液の組成や使用量、マグネシウム化合物の組成などによつても異なる

わかつた。従つて、本発明の目的は改良されたオレフィンの重合方法を提案するにある。

発明の上記目的及び更に多くの他の目的ならびに利点は、以下の記載から一顧明らかとなるであらう。

本発明において、前記オレフィン組成成分(A)の範囲に用いられるマグネシウム化合物(B)は、還元性を有しないマグネシウム化合物、すなわちマグネシウム-酸素錯合やマグネシウム-水素錯合を有しないマグネシウム化合物が好ましく、これらは還元性を有するマグネシウム化合物から誘導されたものであつてもよい。

このような還元性を有しないマグネシウム化合物としては、塩化マグネシウム、臭化マグネシウム、硫化マグネシウム、炭化マグネシウムの様なハロゲン化マグネシウム；メトキシ塩化マグネシウム、エトキシ塩化マグネシウム、イソプロポキシ塩化マグネシウム、ブトキシ塩化マグネシウム、オクトキシ塩化マグネシウムの様なアルコキシマグネシウムハライド；フェノキシ塩化マグネシウム、メチルフェノキシ塩化マグネシウムの様なアリロキシマグネシウムハライド；エトキシマグネシウム、イソプロポキシマグネシウム、ブトキシマグネシウム、ノノキソキシマ

グネシウム化合物の組成などによつても異なる

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が、例えば、ハロゲン含有マグネシウム化合物1モル当り、アルコールを約1モル以上、好ましくは約1.5モル以上、とくに好ましくは2モルを超える範囲で用いられる。同、その上量にはとくに制限はないが、経済的にはその使用量をあまり多くしない方が望ましく、マグネシウム化合物1モル当り、例えばアルコールを約40モル以下、好ましくは約20モル以下、とくに好ましくは約10モル以下とするのがよい。炭化水素として脂肪族炭化水素および又は芳香族炭化水素を使用する場合は、前記割合でアルコールを使用し、そのうちとくに炭数6以上のアルコールを、ハロゲン含有マグネシウム化合物1モルに対し約1モル以上、好ましくは約1.5モル以上用いればアルコールの燃焼効率も僅かでハロゲン含有マグネシウム化合物の可燃化が可能であり、かつ燃焼の大きい熱源成分となるので好ましい。この場合、例えば炭数6以下のアルコールのみを用いると、ハロゲン含有マグネシウム化合物1モルに対し、約1.5モル以上のアルコールが必要であり、燃焼効率も上記系に及

ばない。一方、炭化水素として芳香族炭化水素を用いれば、アルコールの燃焼にかかわらず、前記のようなアルコール使用量でハロゲン含有マグネシウム化合物の可燃化は可能である。さらにナフテン化合物中のうち、テトラアルコキシナフテンのようなものを予め共存させておくと、同様に少量のアルコールで可燃化が可能となる。

ハロゲン含有マグネシウム化合物とアルコールとの燃焼は、炭化水素燃焼中で行うのが好ましく、通常、室温以上、それらの燃焼によつては約50℃以上、好ましくは約90ないし100℃、一層好ましくは約100ないし約200℃の範囲で行うのがよい。燃焼時間も適宜に選択できるが、例えば15分ないし5時間程度、より好ましくは10分ないし2時間程度の燃焼時間を例示できる。アルコールとして好適な炭数6以上のアルコールとしては、例えば2-メチルペンタノール、2-エチルペンタノール、3-ヘキサノール、3-ヘプタノール、2-エチルヘキサノール、デカノール、ドデカノール、テトラデシルアルコール、ウンデセ

ノール、オレイルアルコール、ステアシルアルコールのような脂肪族アルコール；シクロヘキサノール、メチルシクロヘキサノールのような脂環族アルコール；ベンジルアルコール、メチルベンジルアルコール、イソプロピルベンジルアルコール、3-メチルベンジルアルコール、3,3-ジメチルベンジルアルコールなどの芳香族アルコール；α-ブチルセロソルブ、1-ブトキシ-2-プロパノールなどのアルコキシ基を含んだ脂肪族アルコールなどを例示できる。他のアルコールの例としてはメタノール、エタノール、プロパノール、ブタノール、エタレンジリコール、メチルカルビトールの如き炭数6以下のアルコールを例示できる。

また、カルボン酸を使用する場合には、炭数7以上の有機カルボン酸が好適であり、例えばカプリル酸、2-エチルヘキサノイック酸、ウンデシレニック酸、ウンデカノイック酸、ノナノイック酸、オクタノイック酸などを使用することができる。

アルデヒドを使用する場合は、炭数7以上の

アルデヒドが好適であり、例えばカプリツクアルデヒド、2-エチルヘキサノアルデヒド、カプリルアルデヒド、ウンデシツクアルデヒドなどを例示できる。

またアミンを使用する場合には、炭数6以上のものが好適であり例えばヘプタメリン、8-オクタメリン、ノルメリン、デシルアミン、ラウリルアミン、ウンデシルアミン、2-エチルヘキサメリンなどを使用することができる。

又、エーテルを使用する場合には、テトラヒドフランなどを例示することができる。

これらのカルボン酸、アルデヒド、アミンやエーテルを使用する場合の好ましい使用量および燃焼は、アルコールの場合について記述したのと同様である。

本発明において、前記マグネシウム化合物(II)の炭化水素燃焼効率はまだ、前記マグネシウム化合物に炭化し得る他のマグネシウム化合物又はマグネシウム金属を、前記マグネシウム化合物に炭化させつつ燃焼させることにより形成することも可

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ル酸ジローイタール、フタル酸ジトリペンチル、フタル酸ジデシル、フタル酸ベンジル、フタル酸ジフェニル、ナフタリンジカルボン酸ジエチル、ナフタリンジカルボン酸ジブチル、トリノリット酸トリエチル、トリノリット酸ジブチルなどの芳香族ポリカルボン酸エステル、3,4-フランジカルボン酸などの異環族ポリカルボン酸エステルなどを挙げることができる。

また多価ヒドロキシル化合物エステルとして好ましいものの具体例としては、1,2-ジアセトキシベンゼン、1-メチル-2,3-ジアセトキシベンゼン、2,3-ジアセトキシナフタリンなどを挙げることができる。

タタン酸成分中に包含させる多価カルボン酸エステルの他の例としては、アジピン酸ジエチル、アジピン酸ジイソブチル、セバシン酸ジイソブチル、セバシン酸ジローブチル、セバシン酸ジノクタール、セバシン酸ジ-2-エチルヘキシルなどの長鎖ジカルボン酸のエステル類をあげることができる。

0.01ないし約1.0モル、とくに約0.1ないし約0.50モルの割合で用いるのが好ましい。そして固体生成物中に包含されるこれらエステルと電子供与体(D)の比率を、例えば前者1モルに対し、後者を約0.01ないし約2.0モル、とくに約0.1ないし約1.0モルとなるように、両者の使用比率を定めるのが好ましい。

マグネシウム化合物(II)の炭化水素溶液と炭状のタタン化合物(III)の混合物から、マグネシウム及びタタンを含有する固体生成物を形成させるには、両炭状物の反応による手段が好ましい。その際、タタン化合物としてハロゲン含有化合物を使用するとともに固体生成物を形成させるに十分な量で用で用いることが好ましい。タタン化合物(III)の使用量は、その種類、溶解条件や電子供与体(D)その他の使用量によっても異なるが、マグネシウム化合物(II)1モルに対し、約1モル以上、通常約2ないし約200モル、とくに約3ないし約100モルとするのが好ましい。

これら多価カルボン酸エステル又は多価ヒドロキシル化合物エステルを溶解させるに際し、必ずしも出発原料としてこれらを使用する必要はなく、タタン酸成分の純度の過剰でこれらに酸化せしめる化合物を用いて炭酸塩の状態でこれら化合物に酸化せしめてもよい。

前記(II)族又は(III)族において、固体生成物を形成させる段階で存在させる電子供与体(D)の量は、マグネシウム化合物(II)1モルに対し、例えば約0.01ないし約1.0モル、とくに約0.05ないし0.5モルの範囲とすることが望ましい。このような使用量の選択によつて固体生成物の収率を調節することが可能である。

電子供与体(D)の種類によつても異なるが、この量が多すぎると、固体生成物へ多く吸附されすぎて感度を及ぼす場合があり得るので上記例示の範囲で適宜に選択するのが好ましい。

(II)族によつて固体生成物を多価カルボン酸エステル及び/又は多価ヒドロキシル化合物エステルの共存下に形成させる場合、これらエステルは、マグネシウム化合物(II)1モルに対し、例えば約

上記のような事なる段階によつて固体生成物が生じない場合、あるいは(II)と(III)の炭化水素溶液を放置するのみでは固体生成物が生じない場合には、過剰量のタタン化合物(III)、好ましくはハロゲン含有タタン化合物を添加したり、他の析出化剤を添加することによつて固体生成物を形成させることができる。他の析出化剤の一例としては、ハロゲン、ハロゲン化炭化水素、ハロゲン含有キレート化合物、ハロゲン含有アルキル化合物、ハロゲン含有リチウム化合物、ハロゲン含有有機化合物、ハロゲン含有アンモニウム化合物のようなハロゲン化剤を挙げることができる。

固体生成物は、その形成条件によつて形状や大きさなどが異なってくる。形状、粒径などがそろつた固体生成物を得るためには、急激な形成を避けるのが好ましく、例えば(II)と(III)を互いに炭状状態で混合して、相互反応によつて固体生成物を形成させる場合には、それらの段階によつて急激に固体生成物が生じないような充分に低い濃度で両者を混合した後、昇温して徐々に固体生成物を

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形成させるのがよい。この方法によれば、比較的
距離が大きく、粒度分布の狭い顆粒又は塊の
固体生成物が得やすい。

上記の如くにして られる粒度分布が狭な顆粒
状又は塊状の固体組成成分を削いてスラリー重合
や気相重合によつて得られる重合体は、顆粒状又
は塊状で粒度分布、緻密度も大きく、流動性が良
好である。なおここで顆粒状というのは粉末等
でも、恰も微粉末が重合して細くして塊状を
形成しているもので、固体組成成分の割合によつ
て顆粒状物として多数の凹凸があるものから圓球
に近いものまで得ることができる。

なお上記融解において融解温度は、例えば、約
-70℃ないし約+200℃程度の範囲が例示でき
る。融解させるべき両液状物の温度は異なつてい
てもよい。一般には、前記したような顆粒状又は
塊状の好ましい形態でしかも高性量の固体組成成
分を得るには、最速のように両者の混合時にあまり
高温度を適用しない方法を得る方が好ましい場
合が多く、例えば約-70℃ないし約+50℃程度の

中で融解させて固体生成物を含む懸濁液を得る。
一般には、この懸濁液に多価カルボン酸エステル
及び/又は多価ヒドロキシ化合物エステルを添加
し、例えば約0ないし約150℃程度の温度で反応
させる方法が採用される。電子供与体の使用量は
(4)の懸濁液におけるのと同様である。またこのよう
にして得られた固体生成物は、(4)の懸濁液と同様に
液状のタタコン化合物、好ましくは酸化タタコンの
過剰で約20℃ないし約150℃の温度で1回以上
洗浄することができる。

本発明においては、又(4)と(5)の懸濁液を併用する
ことができる。

本発明においては、上記の如き固体生成物の形
成に際して、多孔質の懸濁液及び/又は有機の化合
物を共存させることができ、それによつてこれら
化合物懸濁液に固体生成物を析出させる方法を採
用してもよい。この際、該多孔質化合物は予の液状
状態のマグネシウム化合物と予の懸濁液をさせ、液
状状態のマグネシウム化合物を含む懸濁液に於て
液状のタタコン化合物と融 させることもできる。

融解条件が好ましい。この場合、融解速度が低い
と、塊 状物の析出が速められない場合があり、
そのときは昇温して、例えば好ましくは約50ない
し約150℃に昇温して反応させるか又は長時間
の懸濁によつて固体生成物を析出させるのがよい。
該固体生成物は、好ましくは液状のタタコン化合物
あるいは液状のハロゲン化炭化水素、好ましくは
四塩化タタコンや1,2-ジクロロエタン、クロロベン
ゼン、塩化メチル、ヘキサクロロエタンなどの
過剰で、たとえば、約20ないし約150℃の温
度で1回以上洗浄するのがよい。その後、過剰は
炭化水素で洗浄して重合に使用できる。

この方法は操作が簡単で、しかも高性量の固体
組成成分(A)が得られるので優れた方法である。

本発明において、前記懸濁液(4)の懸濁液においては、
以下のようにして行うことができる。

マグネシウム化合物(1)とタタコン化合物(2)との炭
化水素溶液を形成させた後、あるいは液状状態の
マグネシウム化合物(1)と液状状態のタタコン化合物
(2)とを(4)の懸濁液におけるのと同様な割合および条

件でこれら多孔質化合物の例として、シリカ、アルミ
ナ、ポリオレフィン及びこれ等のハロゲン含有化
合物による結合物などをあけることができる。

本発明の固体タタコン組成成分(A)は、上記(4)や
(5)の懸濁液によつて得られるもの、さらに任意にタ
タコン化合物、炭化水素等で洗浄したものであつて
もよい。

以上の各懸濁液によつて得られる固体タタコン組成
成分(A)は、炭化水素でよく洗浄した後重合に供
するのが好ましい。かくして得られた固体タタコン
組成成分(A)の組成が、マグネシウム/タタコン
(原子比)が例えば約2ないし約100、好ましく
は約4ないし約50、さらに好ましくは約5ないし
約30、ハロゲン/タタコン(原子比)が例えば約4
ないし約100、好ましくは約5ないし約30、さ
らに好ましくは約8ないし約50、電子供与体/タ
タコン(モル比)が例えば約0.01ないし約100、
好ましくは約0.2ないし約10、さらに好ましくは
約0.4ないし約8となつているものが好ましい。ま
たすでに述べたように多くの場合、その形状は圓

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酸又ははば 酸となつてゐる。またその比量由
 量、例えばの $10a^2/8$ 以上、好ましくは約
 100 ないし $1000a^2/8$ の値を示す。

図 4 中酸素成分(A)中のハロゲン、塩素、
 臭素、炭素、臭素あるいはこれら2種以上であり、
 とくに塩素であることが好ましい。また図(A)
 中に含有される電子供与体は、少なくとも多価カ
 ルボン酸エステル又は多価ヒドロキシ化合物エス
 テルから選ばれるものを含んでおり、場合により、
 他に(B)群から選ばれる電子供与体などが含まれ
 ることがある。

多価カルボン酸エステル又は多価ヒドロキシ化
 合物エステルと、その他の電子供与体(B)の含有
 割合は、他の電子供与体(B)の量によつても異
 なるが、前者1モルに対し、後者の電子供与体
 (B)が約2モル以下、好ましくは約1モル以下、
 とくに好ましくは0.5モル以下存在していても良
 好な性質を示す。

本発明においては、以上のようにして得られる
 固体組成成分(A)と、同組成成分(1)ないし(5)

組成成分の有機金属化合物(組成成分(B)及び(C)の
 化合物組成成分(C)の割合を調整を用いてエポ
 キシンの重合または共重合を行う。

同組成成分(1)ないし(5)の有機金属化合物組成成分(B)としては、(1)少なくとも分子内
 に1個のAβ-炭素結合を有する有機アルミニウム
 化合物、例えば一般式



(ここで R^1 および R^2 は炭素原子、通常1ないし
 15個、好ましくは1ないし4個を含む炭化水素基
 で互いに同一でも異なつてもよい。Xはハロゲン、
 a は $0 < a \leq 3$ 、 $0 \leq a < 3$ 、 b は $0 \leq b < 3$ 、
 c は $0 \leq c < 3$ の数であつて、しかも $a+b+c$
 $+d=3$ である)で置換される有機アルミニウム
 化合物、(2)一般式



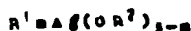
(ここで M^1 はLi、Na、Kであり、 R^1 は前記と同
 じ)で置換される第1金属とアルミニウムとの

図アルキル化合物、(3)一般式



(ここで R^1 および R^2 は前記と同じ。 M^2 はMg、
 Zn、Cdである)で置換される第2金属のジアル
 キル化合物などを挙げることができる。

前記の(1)に属する有機アルミニウム化合物とし
 ては、次のものを例示できる。一般式



(ここで R^1 および R^2 は前記と同じ。 a は好まし
 くは $1.3 \leq a \leq 3$ の数である。)、一般式



(ここで R^1 は前記と同じ。Xはハロゲン、 a は
 好ましくは $0 < a < 3$ である。)、一般式



(ここで R^1 は前記と同じ。 a は好ましくは $1 \leq a$
 < 3 である。)、一般式



(ここで R^1 および R^2 は前記と同じ。Xはハロゲ
 ン、 $0 < a \leq 3$ 、 $0 \leq a < 3$ 、 $0 \leq c < 3$ で、 $a+b+c$
 $+d=3$ である)で置換されるものなどを例示できる。

(1)に属するアルミニウム化合物において、より
 具体的にはトリメチルアルミニウム、トリブチル
 アルミニウムなどのトリアルキルアルミニウム、
 トリイソブチルアルミニウムのようなトリアル
 キルアルミニウム、ジエチルアルミニウムエト
 キシド、ジブチルアルミニウムブトキシドなどの
 ジアルキルアルミニウムアルコキシド、エチルア
 ルミニウムセスキブトキシド、ブチルアルミニ
 ウムセスキブトキシドなどのアルキルアルミニ
 ウムセスキアルコキシドのほか、 $R^1R^2Al(OR^3)_3$
 などで置換される平均組成を有する部分的にアル
 コキシ化されたアルキルアルミニウム、ジエチル
 アルミニウムクロリド、ジブチルアルミニウム
 クロリド、ジエチルアルミニウムブトキシドのよう
 なジアルキルアルミニウムハロゲン、エチルアル
 ミニウムセスキクロリド、ブチルアルミニウムセ
 スキクロリド、エチルアルミニウムセスキブト
 キシドのようアルキルアルミニウムセスキハロゲ
 ン、エチルアルミニウムジクロリド、ブチルア
 ルミニウムジクロリド、ブチルアルミニウムジ

又、従来 薬品では混合時間の経過に伴ない結性の低下が生じるが、本組成系では、ほとんどそれも認められない為、例えば多量遠心分離での使用において混合作業量 大なるアツプにつながる。

又、本組成系は高濃度においても非常に安定な為、例えばプロピレンの重合を90℃で行つても立体的結性の低下はあまり認められない。

次に実験例によりさらに詳細に説明する。

実 施 例 1

(固体T1組成成分(A)の調製)

無水塩化マグネシウム 4.76g (50mmol)、
チタン 25mg および2-エチルヘキシルアルコール 23.4g (150mmol) を130℃で2時間加熱反応を行い均一溶液とした後、この溶液中に無水フタル酸 1.11g (7.5mmol) を添加し、130℃にて更に1時間加熱混合を行い、無水フタル酸を均一溶液に溶解させる。この液にして得られた均一溶液を密閉に冷却した後、-20℃に保持され

750mg を投入し、密閉下プロピレン雰囲気にてトリエチルアルミニウム 2.51mmol、フェニルトリエチルシリラン 0.175mmol 及び前記組成成分(A)をチタン原子換算で0.015mmol投入した。水素 200mg を導入した後、70℃に昇温し、2時間のプロピレン重合を行つた。重合中の圧力は7kg/cm²に保つた。

重合終了後、生成重合体を含むスラリーを引出し、白色粉末状重合体と液相部に分離した。液相部の白色粉末状重合体の収量は379.2gであり、液とろーへフタンによる抽出率は98.9%、 η_{sp} は7.3、その見掛け粘度は0.14g/cm²であつた。又、白色粉末状重合体の粒度分布は表1に示すとおりであつた。一方、液相部の固形により得られる重合体 1.9g を得た。従つて得率は29.400g-PP/mol-Tiであり、全重合体に対するTiは98.4%であつた。

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に四塩化チタン 200mg (1.4mmol) 中に1時間に亘つて全量導入する。導入終了後、この重合体の温度を4時間かけて110℃に昇温し、110℃に達したところでジイソブチルマタレート 2.68mg (12.5mmol) を添加し、これより2時間同温度にて固相下保持する。2時間の反応終了後液相部にて固相部を採取し、この固相部を200mgのT100にて再溶解させた後、再び110℃で2時間、加熱反応を行う。反応終了後、再び液相部にて固相部を採取し、110℃チタン及びヘキサンにて、液相中に溶解のチタン化合物が抽出されなくなる迄充分洗浄する。以上の操作方式にて合成された固体T1組成成分(A)はヘキサンスラリーとして保存するが、このうち一試を組成測定を目的で乾燥する。この値にして得られた固体T1組成成分(A)の組成はチタン 5.1重量%、塩素 56.0重量%、マグネシウム 17.0重量% およびジイソブチルマタレート 20.9重量%であつた。

(組 合)

内蔵量 2g のオートクレーンに前記ヘキサン

表 1

>1190 μ	>840 μ	>420 μ	>250 μ	>177 μ
0	0	4.1	95.7	0.2

>105 μ	>64 μ	64 μ >
0	0	0

実施例 2, 3, 4, 5, 6

実施例1の組成成分(A)を用い、重合に用いる水素の添加量を100mg、400mg、800mg、1000mg、2000mgに改えた以外は実施例1と同様にして重合を行つた。重合結果を表2に示した。

第 2

実施例	水素の添加量 n g	n l	価 値 $(\text{g-P}/\text{mg}) - \text{P}$	白色粉末状量 合計の 11 g	全量介体に おける 11 g
実施例 2	100	7.7	20.000	98.9	98.4
・ 1	200	7.5	25.400	98.9	98.4
・ 3	400	7.0	30.800	98.6	98.0
・ 4	800	6.9	32.100	98.3	97.7
・ 5	1000	14.5	34.000	97.7	97.0
・ 6	2000	28.0	29.600	97.4	96.6

実 施 例 7 . 8

実施例 1 の樹脂成分(A)を用い、重合温度を 80℃、90℃に変えた以外は実施例 1 と同様にして重合を行った。重合結果を表 3 に示した。

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10

内容積2 lのオートクレーブに硝酸ヘキサン 750 ml を加入し、窒素プロピレン蒸気流下でトリメチルアルミニウム 7.51 mmol、フェニルトリメトキシシラン 0.225 mmol 及び実施例 1 配の触媒成分(A)をセタン原子量で 0.015 mmol 加入した。水素 200 ml を導入した後、70℃に昇出し2時間のプロピレン重合を行った。反応中の圧力は7 kg/cm²に保った。以下実施例 1 配製と同様な操作により、低介体の重合を行った。結果を表5に示した。

興 興 興 17

内容物2gのオートクレーブに精製ヘキサン750mlを装入し、窒素雰囲気下でトリエチルアルミニウム2.51mmol、ビニルトリノトキシシラン0.50mmol及び変換例1記載の触媒成分(A)をセタン磁子攪拌で0.015mmol装入した。

750mgを投入し、有機プロピレン雰囲気下でトリ
エチルアルミニウム 2.51mmol、タトラエトキシ
シラン 0.30mmol 及び実施例1記載の触媒成分
(A) をセタン原子換算で 0.015mmol 投入した。
水素 200mg を導入した後、70℃に昇温し、4時
間のプロピレン重合を行った。重合中の圧力は
7kg/cm²に保った。以下実施例1記載と同様な操
作により、重合部の後処理を行った。結果を表
に示した。

20 總 覽

内容物2gのオートクレーブに無水ヘキサン750mgを注入し、高圧プロピレン雰囲気下でトリエチルアルミニウム7.51mmol、エチルトリエトキシラン0.225mmol及び触媒1記量の触媒成分(A)をセタン原子量で0.015mmol投入した。本液200mgを過入した後、70℃に昇温し、4時間のプロピレン重合を行った。重合の圧力は7MPaに保った。以下触媒1記量と触媒成分により、重合後の触媒回収を行った。触媒を

740551-43006 (15)

本装置200mgの塩素化した酸、70℃に昇温し、4時間のプロピレン重合を行った。重合中の圧力は744/ mm^2 に保った。以下が実験例1と酸と同等な操作により、重合体の数値特性を行った。結果を表1に示した。

100

内容物2gのオートクレーブに硝酸ヘキサン750mgを投入し、窒素プロピレン置換気下でトリエチルアルミニウム2.51mmol、メチルトリイソシシラン0.65mmol及び炭酸銅(Ⅱ)配体の無水成分(A)をチタン原子当量で0.015mmol投入した。水素200mgを導入した後、70℃に昇温し、2時間のプロピレン重合を行った。重合中の圧力は7kg/cm²に保った。以下炭酸銅(Ⅱ)配体と同様な操作により、重合体の製造を行った。結果を表5に示した。

寶 鼎 銅 人

内市販2位のオートクレーブに殺菌へキサン

書くに示して、

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内容量2 lのオートクレーブに特製ヘキサン750 mlを投入し、窒素プロピレン雰囲気下でトリエチルアルミニウム2.51 mmol、ピニトリエリシラン0.225 mmol及び実施例1記載の触媒成分(A)をサチン原子量で0.015 mmol投入した。本量200 mlを投入した後、70℃に昇温し、4時間のプロピレン重合を行った。重合中の圧力は74/100 mmHgに保った。以下実施例1記載と同様な操作により、重合体の製造を行った。結果を表5に示した。

雙 龍 洞 22

内容物 2.8 のオートクレーブに精糖ヘキサン 250 mg を投入し、窒素プロピレン雰囲気下でトリエチルアルミニウム 2.5 mmol、ジメチルエチルジメチルラン 0.225 mmol 及び炭素 1 配位錯体配合物 (A) をサタン分子量で 0.015 mmol 調

実 施 例 24

(固体T1組成成分(A)の調製)

無水塩化マグネシウム 4.76g (50mmol) ユ
 カン 23.4g および 2-エチルヘキシルアルコール
 23.4g (150mmol) を 150℃ で 2 時間加熱反応
 を行い均一溶液とした後、この溶液中に無水フタ
 ル酸 1.11g (7.5mmol) を添加し、150℃ にて並
 に 1 時間加熱混合を行い無水フタル酸を均一溶
 液に溶解させる。この液にして得られた均一溶液
 を室温に冷却した後、-20℃ に保持された四塩化
 タン 200mg (1.5mmol) 中に 1 時間に亘つて全
 量滴下投入する。投入終了後、この混合液の温度
 を 4 時間かけて 110℃ に昇温し、110℃ に達した
 ところでジノルマルアトルフラート 3.5g
 (12.5mmol) を添加し、これより 2 時間同温度に
 保持する。2 時間の反応終了後、反応物より無溶
 媒にて固体部を採取し、この固体部を 200mg の
 T1C₆ にて再溶解させた後、再び 120℃ で 2 時
 間、加熱反応を行う。反応終了後、再び無溶媒に
 て固体部を採取し、120℃ でカン及びヘキサンに

化タン 200mg (1.5mmol) 中に 1 時間に亘つて
 全量滴下投入する。投入終了後、この混合液の温
 度を 4 時間かけて 110℃ に昇温し、110℃ に達し
 たところでジエチルフラート 2.6g (15.0mmol)
 を添加し、これより 2 時間同温度に保持する。2
 時間の反応終了後、反応物より無溶媒にて固体部
 を採取し、この固体部を 200mg の T1C₆ にて再
 溶解させた後、再び 120℃ で 2 時間加熱反応を行
 う。反応終了後、再び無溶媒にて固体部を採取し
 120℃ でカン及びヘキサンにて脱液中に遊離のタ
 ン化合物が抽出されなくなる迄ヘキサンで
 充分洗浄する。以上の製造方法にて合成された固
 体 T1 組成成分(A)はヘキサン溶液として保
 存するが、このうち一部を触媒組成を調べる目的
 で試験を行う。この液にして得られた固体 T1 組成
 成分(A)の含有量は 4.0wt% であつた。

上記固体 T1 組成成分(A)を使用して実施例
 1 に記載の法 によりプロピレン重合を行つた。
 重合を促進した。

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で、脱液中の遊離のタン化合物が抽出されなく
 なる迄ヘキサンで充分洗浄する。以上の製造
 方法にて合成された固体 T1 組成成分(A)はヘ
 キサン溶液として保存するが、このうち一部を
 触媒組成を調べる目的で試験を行う。この液に
 して得られた固体 T1 組成成分(A)のタン含有量
 は 7.1 wt% であつた。上記固体 T1 組成成分(A)
 を使用して、実施例 1 に記載の操作によりプロ
 ピレン重合を行つた。重合結果を後示した。

実 施 例 25

(固体T1組成成分(A)の調製)

無水塩化マグネシウム 4.76g (50mmol) ユ
 カン 23.4g および 2-エチルヘキシルアルコール
 23.4g (150mmol) を 150℃ で 2 時間加熱反応
 を行い均一溶液とした後、この溶液中に無水フタ
 ル酸 1.11g (7.5mmol) を添加し、150℃ にて並
 に 1 時間加熱混合を行い、無水フタル酸を均一
 溶液に溶解させる。この液にして得られた均一溶
 液を室温に冷却した後、-20℃ に保持された四塩

実 施 例 26

(固体T1組成成分(A)の調製)

無水塩化マグネシウム 4.76g (50mmol)、
 デカン 23.4g および 2-エチルヘキシルアルコ
 ル 23.4g (150mmol) を、150℃ で 2 時間加熱
 反応を行い均一溶液とした後、この溶液中に無水
 フタル酸 1.11g (7.5mmol) を添加し、150℃ に
 て並に 1 時間加熱混合を行い無水フタル酸を均
 一溶液に溶解させる。この液にして得られた均一
 溶液を室温に冷却した後、-20℃ に保持された四
 塩化タン 200mg (1.5mmol) 中に 1 時間に亘つ
 て全量滴下投入する。投入終了後、この混合液の
 温度を 4 時間かけて 110℃ に昇温し、110℃ に達
 したところでジイソプロピルフラート 2.9g
 (12.5mmol) を添加し、これより 2 時間同温度に
 保持する。2 時間の反応終了後、反応物より無溶
 媒にて固体部を採取し、この固体部を 200mg の
 T1C₆ にて再溶解させた後、再び 120℃ で 2 時
 間加熱反応を行う。反応終了後、再び無溶媒に
 て固体部を採取し、120℃ でカン及びヘキサンにて

反応に遊離のチオン化合物が放出されなくなる迄、遊離ヘキサンで充分洗淨する。以上の製造方法にて合成された固体T1触媒成分(A)はヘキサンスラリーとして保存するか、このうち一部を触媒組成を調べる目的で試験を行う。この際にして得られた固体T1触媒成分(A)のTi含有量は2.9%であった。

上記固体T1触媒成分(A)を使用して実験例1に記載の操作によりプロピレン重合を行った。重合結果を後述に示した。

実 験 例 27

(固体T1触媒成分(A)の調製)

無水塩化マグネシウム4.76g(50mmol)、チカン25mgおよび2-エチルヘキシルアルコール23.4g(150mmol)を、150℃で2時間加熱反応を行い均一溶液とした後、この溶液中に無水フタル酸1.11g(7.5mmol)を添加し、150℃にて更に1時間攪拌混合を行い無水フタル酸を均一溶液に溶解させる。この際にして得られた均一溶

15に記載の操作によりプロピレン重合を行った。重合結果は、活性16,300g-PP/mol-Tiであり、全重合体に対するTiは96.5%、その見掛け密度は0.47g/cm³であった。

又、無固体触媒成分を調もつてトリエチルアルミニウム及びジフェニルジメチルシランと試験させた後実験例15に記載の操作よりプロピレン重合を行った。試験条件を次に示す。

H₂置換を施した400mlフラスコ中に無水ヘキサン200ml、トリエチルアルミニウム30mmol、ジフェニルジメチルシラン60mmol及び無固体触媒成分をTi原子当量で5mmol投入した後、プロピレンを1時間6.6g/Hrの流速で反応器内に投入した。同この間の温度は25℃以下に保持した。1時間経過後プロピレンの投入を止め系内をH₂で十分に置換した。更に全反応物をタイラー上に移し、無固体のみを回収した後、無固体を無水ヘキサンにリステリーし重合に使用した。重合結果を後述に示す。

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液を室温に冷却した後、-20℃に冷却され、内電化チカン200mg(1.8mmol)中に1時間攪拌して全量溶解する。同量終了後、この混合物の温度を4時間かけて110℃に昇温し、110℃に達したところでジエチルアルミニウム2.9mg(12.8mmol)を添加し、これより2時間同温度に保持する。2時間の反応終了後、反応物より無固体を回収し、この無固体を200mgのTiCl₄にて再処理させた後、再び120℃で2時間加熱反応を行う。反応終了後、再び無固体を回収し、120℃でチカン及びヘキサンにて反応中に遊離のチオン化合物が放出されなくなる迄、遊離ヘキサンで充分洗淨する。以上の製造方法にて合成された固体T1触媒成分(A)はヘキサンスラリーとして保存するか、このうち一部を触媒組成を調べる目的で試験を行う。この際にして得られた固体T1触媒成分(A)のTi含有量は3.9%であった。

(重合)

上記固体T1触媒成分(A)を使用して実験例

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無機物成分(A)のTi含有率は5.1wt%であった。
(註)

無機物成分(A)を用い実施例15と同様な操作によりプロピレン重合を行った。結果を表8に示す。

実施例 37

(図 表 1 無機物成分(A)の調製)

実施例1に記載の無水フタル酸 1.11g

(7.5mmol)をn-ブチルセロソルブ0.99ml

(7.5mmol)に置いた以外は全て実施例1に記載の操作により無機物成分(A)を合成した。無機物成分(A)のTi含有率は5.5wt%であった。

(註 合)

無機物成分(A)を用い実施例15と同様な操作によりプロピレン重合を行った。結果を表8に示す。

実施例 38

1.11gの無水フタル酸 1.11g
実施例15と同様な操作により無機物成分(A)を合成した。

(註 合) (7.5mmol)をn-ブチルセロソルブ0.99ml (7.5mmol)に置いた以外は全て実施例1に記載の操作により無機物成分(A)を合成した。無機物成分(A)のTi含有率は5.1wt%であった。無機物成分(A)を用い実施例15と同様な操作によりプロピレン重合を行った。結果を表8に示す。

表 8

実施例	活 性 R-PP/Amol-Ti	Ti %	M1	無機物 %	融 点 分 布 (%)							
					>1100°	>840°	>420°	>250°	>177°	>105°	>44°	44°以下
30	25.200	97.6	8.1	0.43	0	0	0	4.7	56.8	37.7	0.3	0
31	25.400	97.4	4.1	0.40	0	0	0	5.0	79.4	15.7	0.4	0
32	17.700	97.8	2.4	0.35	0	0	0.4	94.4	3.8	1.0	0	0
33	25.100	97.3	3.1	0.43	0	0	0	0.3	4.4	39.7	35.6	0
34	31.100	97.3	3.2	0.37	0	0	0	10.2	44.1	41.3	0.4	0
35	16.300	98.1	1.9	0.37	0	0.2	0.0	0.9	01.3	8.6	0.2	0
36	8.400	99.7	4.8	0.44	0	0	0	0.8	2.8	56.4	40.7	0
37	17.100	98.6	1.5	0.36	0	0	0.3	5.1	52.4	40.9	1.3	0
38	22.400	97.7	3.5	0.41	0	0.3	30.9	40.3	0.3	0	0	0

附録 58-03000 (22)

資料 59

5でAつた。

内容物 7 のオートクレーブに精製ヘキサン
 750 g を投入し、室温下プロピレンを飽和すにて
 トリエチルアルミニウム 2.51 mmol、フェニル
 イソシラン 0.15 mmol 及び有機銅 1 当量
 成分 (A) をチタン原子換算で 0.015 mmol 投入
 した。本量 100 g を投入した後 60℃ に昇温し、
 混合系の温度が 60℃ に到達したところでエチレン
 を 8.1 mmol を含むプロピレン-エチレン混合ガス
 を供給し混合圧力を 2 kg/cm² に 2 時間保った。
 反応終了後、生成物混合物を含むスラリーを押し出し
 白色粉末状混合物と液体部に分離した。反応後の
 白色粉末状混合物の収量は 273.2 g であり、MI
 は 0.9、その見掛け密度は 0.37 g/cm³ であつた。又
 白色粉末状混合物中には 5.0 mmol の異立エチレン
 が存在している事を 1H NMR 測定により確認
 し、更に DSC により、この混合物の T_g が 155℃
 である事を確認した。一方液体部の蒸留により溶
 媒可溶性混合物 14.8 g を得た。従つて総量は
 19.200 g - P₂/mmol-TI であり、収率は 94.9

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CLAIMS:

1. A process for producing olefin polymers or copolymers which comprises polymerizing olefins or copolymerizing olefins in the presence of a catalyst composed of the following components (A), (B), and (C):

(A) a solid titanium catalyst component containing magnesium, titanium, halogen and an ester of polycarboxylic acids, said catalyst component being obtained by (1) contacting a liquid hydrocarbon solution of (i) a magnesium compound having no reducing ability, the hydrocarbon solution being obtained by mixing the magnesium compound and the hydrocarbon with or without heating the mixture, or by mixing a magnesium compound and the hydrocarbon in the presence of an alcohol with or without heating the mixture, with (ii) a tetravalent titanium compound of the formula $Ti(OR)_4$ wherein R represents a hydrocarbon group, X represents a halogen atom and g is a number represented by 0.1 to 0.4 in the liquid state to form a solid product or (2) first preparing a liquid hydrocarbon solution of the magnesium compound (i) and the titanium compound (ii) and then forming a solid product therefrom, by adding an additional amount of the titanium compound (ii) or a precipitating agent selected from the group consisting of halogens, halogenated hydrocarbons, halogen-containing silicon compounds, halogen-containing aluminum compounds, halogen-containing lithium compounds, halogen-containing sulfur compounds and halogen-containing antimony compounds, said reaction of forming the solid product being carried out in the presence of (D) at least one electron donor selected from the group consisting of C2 - C20 monocarboxylic acid esters, C1 - C20 aliphatic carboxylic acids, C4 - C20 carboxylic acid anhydrides, C3 - C20 ketones, C3 - C20 aliphatic carbonates, C3 - C20 alkoxy group-containing alcohols and organic silicon compounds having an Si-O-C bond in which the organic group has 1 to 10 carbon atoms, and during or after the formation of the solid product, contacting the solid product with (E) an ester of polycarboxylic acid selected from the group consisting of C5 - C30 aliphatic polycarboxylic acid esters, C10 - C30 alicyclic polycarboxylic acid esters, C10 - C30 aromatic polycarboxylic acid esters and C8 - C30 heterocyclic polycarboxylic acid esters, wherein the amount of said at least one electron donor (D) is about 0.05 to about 0.5 mole per mole of magnesium compound (i) and the amount of said ester of polycarboxylic acid (E) is about 0.1 to about 0.5 mole per mole of magnesium compound (i), (B) an organoaluminum compound catalyst component, and (C) an organic silicon compound catalyst component having an Si-O-C bond.

Discriptions

This invention relates to a process for producing olefin polymers (sometimes used to denote both homopolymers and copolymers of olefins) by the polymerization (sometimes used to denote both homopolymerization and copolymerization) of olefins. Particularly, it relates to a process for producing olefins polymers of high stereospecificity in large quantities by the polymerization of alpha-olefins having at least 3 carbon atoms.

In the polymerization of alpha-olefins having at least 3 carbon atoms according to the process of the invention, the resulting polymer shows little or no reduction in stereospecificity even when the melt index of the polymer is changed by using a molecular weight controlling agent such as hydrogen. Furthermore, when the process of this invention is carried out by the slurry polymerization method or vapor phase polymerization method, there can be obtained a granular or spherical polymer which has good flowability, a high bulk density, and a narrow particle size distribution with most of the particles having a moderate particle size. The process of this invention also has the advantage that the decrease of the activity of the catalyst is extremely little with the lapse of the polymerization time.

More specifically, this invention relates to a process for producing olefin polymers or copolymers which comprises polymerizing or copolymerizing olefins or copolymerizing olefins and dienes in the presence of a catalyst system composed of the following components (A), (B) and (C):

(A) a solid titanium catalyst component containing magnesium, titanium, halogen and an

ester selected from the group consisting of esters of polycarboxylic acids and esters of polyhydroxy compounds, said catalyst component being obtained by contacting a liquid hydrocarbon solution of (i) a magnesium compound with (ii) a titanium compound in the liquid state to form a solid product or first preparing a liquid hydrocarbon solution of the magnesium compound (i) and the titanium compound (ii) and then forming a solid product therefrom, said reaction of forming the solid product being carried out in the presence of (D) at least one electron donor selected from the group consisting of monocarboxylic acid esters, aliphatic carboxylic acids, carboxylic acid anhydrides, ketones, aliphatic ethers, aliphatic carbonates, alkoxy group-containing alcohols, aryloxy group-containing alcohols, organic silicon compounds having an Si--O--C bond and organic phosphorus compounds having a P--O--C bond, and during or after the formation of the solid product, contacting the solid product with (E) an ester selected from the group consisting of esters of polycarboxylic acids and esters of polyhydroxy compounds.

(B) an organometallic compound of a metal selected from the group consisting of metals of Groups I to III of the periodic table, and

(C) an organic silicon compound having an Si--O--C bond or Si--N--C bond.

This invention also pertains to the aforesaid solid titanium catalyst component.

Numerous techniques have been proposed heretofore about the production of a solid catalyst component consisting essentially of magnesium, titanium, halogen and an electron donor, and it is known that the use of this solid catalyst component in the polymerization of alpha-olefins having at least 3 carbon atoms can give highly stereospecific polymers with high catalytic activity. Many of these prior techniques, however, are still desired to be improved in regard to the activity of the catalyst component and the stereospecificity of the polymer.

For example, in order to obtain an olefin polymer of high quality without the need to treat it after the polymerization, the proportion of a stereospecific polymer formed should be very high and the yield of the polymer per unit amount of the transition metal should be sufficiently high. From this viewpoint, the prior techniques may be on a fairly high level with certain types of polymer, but few are entirely satisfactory in regard to the residual halogen content of the polymer which causes the corrosion of molding machines. In addition, many of the catalyst components produced by the prior techniques have the defect of reducing yield and stereospecificity to not a small extent.

Japanese Laid-Open Patent Publication No. 94590/1979 (laid open on Jul. 26, 1979) discloses a process for polymerizing olefins using a catalyst system containing a compound which can overlap the component (C) of the catalyst system used in this invention. This patent document, however, fails to disclose the component (A) specified in the present application. Japanese Laid-Open Patent Publication No. 36203/1980 (laid-open on Mar. 13, 1980) also discloses a process for polymerizing olefins using a catalyst system containing a compound which can overlap the component (C) used in this invention, but fails to disclose the catalyst component (A).

Japanese Laid-Open Patent Publication No. 811/1981 laid open on Jan. 7, 1981 (corresponding to U.S. Pat. No. 4,330,649) of which inventorship includes the present inventors discloses a process for the production of olefin polymers or copolymers having good flowability, a uniform particle size and a uniform particle size distribution, which is especially suitable for the polymerization of alpha-olefins having at least 3 carbon atoms. This patent is quite silent on the use of a polycarboxylic acid ester and/or an ester of a polyhydroxy compound as an electron donor in the formation of a solid titanium catalyst component. Furthermore, it fails to disclose anything about the combined use of such an ester and the aforesaid electron donor (D), and the combined use of these with the organic silicon compound (C).

The present inventors made extensive investigations in order to provide a further improved process for polymerizing olefins. These investigations have led to the discovery that by using a new type of catalyst system composed of the titanium catalyst component (A) prepared by using both the electron donor (D) and the ester (E) selected from esters of

polycarboxylic acids and esters of polyhydroxy compounds, and the aforesaid components (B) and (C), polymers having excellent quality in respect of particle size, particle size distribution, particle shape and bulk density can be obtained with high catalytic performance and a very little decrease in activity with the passage of the polymerization time. It has also been found that the process of this invention reduces the prior art's defect that an attempt to obtain a polymer of a high melt index by performing the polymerization in the presence of a molecular weight controlling agent such as hydrogen results in not a small reduction in stereospecificity. It has further been found that the use of a small amount of hydrogen makes it possible to adjust the melt index of the polymer. The present invention also brings about the unexpected advantage that by the use of a molecular weight controlling agent such as hydrogen, the activity of the catalyst rather increases.

It is an object of this invention therefore to provide an improved process for polymerizing olefins.

The above and other objects and advantages of this invention will become more apparent from the following description.

The magnesium compound (i) used in the preparation of the solid titanium catalyst component (A) in this invention is preferably a magnesium compound having no reducing ability, i.e. a magnesium compound free from a magnesium-carbon bond or magnesium-hydrogen bond. Such a magnesium compound may be derived from a magnesium compound having reducing ability.

Illustrative of the magnesium compound having no reducing ability are magnesium halides such as magnesium chloride, magnesium bromide, magnesium iodide and magnesium fluoride; alkoxy magnesium halides, for example C1 -C10 alkoxy magnesium halides such as methoxy magnesium chloride, ethoxy magnesium chloride, isopropoxy magnesium chloride, butoxy magnesium chloride and octoxy magnesium chloride; aryloxy magnesium halides, for example phenoxy magnesium halides which may optionally be substituted by lower alkyl groups, such as phenoxy magnesium chloride and methylphenoxy magnesium chloride; alkoxy magnesiums, for example C1 -C10 alkoxy magnesiums such as ethoxy magnesium, isopropoxy magnesium, butoxy magnesium, n-octoxy magnesium and 2-ethylhexoxy magnesium; aryloxy magnesiums, for example phenoxy magnesiums which may optionally be substituted by lower alkyl groups; and magnesium salts of carboxylic acids, for example magnesium salts of aliphatic carboxylic acids having 1 to 20 carbon atoms, such as magnesium laurate and magnesium stearate. The magnesium compounds may be in the form of complexes or mixtures with other metals. The halogen-containing magnesium compounds, above all magnesium chloride, alkoxy magnesium chlorides and aryloxy magnesium chlorides, are preferred among these magnesium compounds.

In preparing the liquid hydrocarbon solution of the magnesium compound (i), various hydrocarbon solvents can be used. Examples include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, tetradecane and kerosene; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, cyclooctane and cyclohexene; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene and cymene; and halogenated hydrocarbons such as dichloroethane, dichloropropane, trichloroethylene, carbon tetrachloride and chlorobenzene.

The solution may be prepared by various methods chosen depending upon the types of the magnesium compound and the solvent, for example by simply mixing the two; mixing the two and heating the mixture; or mixing the magnesium compound with the hydrocarbon solvent in the presence of, or after being treated with, an electron donor capable of solubilizing the magnesium compound, such as an alcohol, an aldehyde, a carboxylic acid, an ether or a mixture thereof, or a mixture thereof with another electron donor, and as required, heating the mixture.

For example, in the case of dissolving a halogen-containing magnesium compound (i) in the hydrocarbon solvent with the aid of an alcohol, the alcohol may be used in an amount of at least about 1 mole, preferably at least about 1.5 mole, especially preferably more than

2 moles, per mole of the halogen-containing magnesium compound although the molar ratio of these may be varied properly depending upon the type and amount of the hydrocarbon solvent and the type of the magnesium compound. There is no particular upper limit to the amount of the alcohol, but economically, it is desirable not to use it in too large an amount. For example, the amount of the alcohol is up to about 40 moles, preferably up to about 20 moles, especially preferably up to about 10 moles, per mole of the magnesium compound (i). When an aliphatic or alicyclic hydrocarbon is used as the hydrocarbon solvent, alcohols are used in the above-mentioned proportion, and among them, alcohols having at least 6 carbon atoms are used in an amount of at least about 1 mole, preferably at least about 1.5 moles, per mole of the halogen-containing magnesium compound. This is preferred since the halogen-containing magnesium compound can be solubilized with the use of alcohols in a small total amount and a catalyst component having high activity can be prepared. If in this case only alcohols having not more than 5 carbon atoms are used, their amount should be at least about 15 moles per mole of the halogen-containing magnesium compound, and the resulting catalyst component has lower catalytic activity than that obtained as described above. On the other hand, when an aromatic hydrocarbon is used as the hydrocarbon solvent, the halogen-containing magnesium compound can be solubilized by using alcohols in the aforesaid amounts irrespective of the types of the alcohols. Furthermore, if, for example, a tetraalkoxy titanium is caused to be present together as the titanium compound (ii) in solubilizing the halogen-containing magnesium compound, the use of a small amount of alcohols makes it possible to solubilize the halogen-containing magnesium compound.

Preferably, the contacting of the halogen-containing magnesium compound with the alcohols is carried out in a hydrocarbon medium usually at room temperature or a higher temperature, and depending upon the types of these compounds, at more than about 65 DEG C., preferably about 80 DEG to about 300 DEG C., more preferably at about 100 DEG to about 200 DEG C. The contact time can also be properly selected. For example, it is about 15 minutes to about 5 hours, preferably about 30 minutes to about 2 hours. Illustrative of suitable alcohols having at least 6 carbon atoms are C₆-C₂₀ aliphatic alcohols such as 2-methylpentanol, 2-ethylbutanol, n-heptanol, n-octanol, 2-ethylhexanol, decanol, dodecanol, tetradecyl alcohol, undecanol, oleyl alcohol and stearyl alcohol; C₆-C₂₀ alicyclic alcohols such as cyclohexanol and methylcyclohexanol; C₇-C₂₀ aromatic alcohols such as benzyl alcohol, methylbenzyl alcohol, isopropylbenzyl alcohol, alpha-methylbenzyl alcohol and alpha, alpha-dimethylbenzyl alcohol; and C₆-C₂₀ aliphatic alcohols containing an alkoxy group, such as n-butyl Cellosolve (=ethylene glycol mono-n-butyl ether) and 1-butoxy-2-propanol. Examples of other alcohols are alcohols having not more than 5 carbon atoms such as methanol, ethanol, propanol, butanol, ethylene glycol and methyl carbitol.

When the carboxylic acid is used as an electron donor, organic carboxylic acids having at least 7 carbon atoms are suitable. Examples include those having 7 to 20 carbon atoms, such as caprylic acid, 2-ethylhexanoic acid, undecylenic acid, undecanoic acid, nonylic acid and octanoic acid.

Suitable aldehydes for used as the electron donor are those having at least 7 carbon atoms. Examples are those having 7 to 18 carbon atoms, such as capric aldehyde, 2-ethylhexyl aldehyde, capryl aldehyde and undecylic aldehyde.

Suitable amines are those having at least 6 carbon atoms. Examples include amines having 6 to 18 carbon atoms, such as heptylamine, octylamine, nonylamine, decylamine, laurylamine, undecylamine and 2-ethylhexylamine.

Illustrative of the ether as the electron donor is tetrahydrofuran.

The preferred amounts of these carboxylic acids, aldehydes, amines and ethers and the preferred temperatures at which they are used are much the same as described hereinabove.

The hydrocarbon solvent solution of the magnesium compound (i) may also be formed by using magnesium metal or another magnesium compound capable of being converted to the magnesium compound (i), and dissolving it in the hydrocarbon solvent while converting

it to the magnesium compound (i). For example, this can be achieved by dissolving or suspending a magnesium compound having an alkyl, alkoxy, aryloxy, acyl, amino or hydroxyl group, magnesium oxide, or metallic magnesium in a hydrocarbon solvent having the alcohol, amine, aldehyde, carboxylic acid, ether, etc. dissolved therein, and forming a halogen-containing magnesium compound (i) having no reducing ability while halogenating it with a halogenating agent such as a hydrogen halide, a halogen-containing silicon compound, halogen, a halogen-containing aluminum compound, a halogen-containing lithium compound or a halogen-containing sulfur compound. Alternatively, it is possible to treat a Grignard reagent, a dialkyl magnesium, magnesium hydride or a complex of such a magnesium compound with another organometallic compound, for example a magnesium compound having reducing ability represented by the formula $M.\alpha.\beta.R@1p.R@2q.Xr.Ys$ wherein M represents aluminum, zinc, boron or beryllium, R@1 and R@2 represent a hydrocarbon group, X and Y represent a group of the formula $OR@3.OSiR@4.R@5.R@6.NR@7.R@8$ or $SR@9$, R@3, R@4, R@5, R@6, R@7 and R@8 represent a hydrogen atom or a hydrocarbon group, R@9 represents a hydrocarbon group, α and β are greater than zero, p, q, r and s are a number of at least 0, m represents the atomic valence of M, $\beta/\alpha \leq 0.5$, $p+q+r+s=m.\alpha.+2.\beta.$, and $0 \leq (r+s)/(\alpha+\beta) < 1.0$ with a compound capable of destroying reducing ability, such as an alcohol, a ketone, an ester, an ether, an acid halide, a silanol, a siloxane, oxygen, water, an acetal, or an alkoxy or aryloxy compound of silicon or aluminum, and dissolving the resulting magnesium compound (i) having no reducing ability in the hydrocarbon solvent. <#s> In the above formula, examples of the hydrocarbon groups are C1 to C20 alkyl groups such as an ethyl group, propyl group, butyl group, amyl group, hexyl group, octyl group and dodecyl group, and C6 to C20 aryl groups such as a phenyl group and tolyl group.

Various titanium compounds can be used as the titanium compound (ii) in the preparation of the solid titanium catalyst component (A). Preferred are tetravalent titanium compounds of the formula

$$Ti(OR)_gX_{4-g}$$

wherein R represents a hydrocarbon group, X represents a halogen atom and g is a number represented by $0 \leq g \leq 4$. In the above formula, examples of the hydrocarbon group are C1 - C10 alkyl groups, and a phenyl group which may have a substituent such as a lower alkyl group, for example C1 to C4 alkyl group, and a halogen atom.

Specific examples of the titanium compound (ii) include titanium tetrahalides such as $TiCl_4$, $TiBr_4$ and TiI_4 ; alkoxy titanium trihalides such as $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(On-C_4H_9)Cl_3$, $Ti(OC_2H_5)Br_3$ and $Ti(On-C_4H_9)Br_3$; alkoxy titanium dihalides such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(On-C_4H_9)_2Cl_2$ and $Ti(OC_2H_5)_2Br_2$; trialkoxy titanium monohalides such as $Ti(OCH_3)_3Cl$, $Ti(OC_2H_5)_3Cl$, $Ti(On-C_4H_9)_3Cl$ and $Ti(OC_2H_5)_3Br$; tetraalkoxy titaniums such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$ and $Ti(On-C_4H_9)_4$; mixtures of these; and mixtures of these with hydrogen halides, halogens, other metallic compounds such as aluminum compounds or silicon compounds, or sulfur compounds. Of these, halogen-containing titanium compounds are preferred. Titanium tetrahalides, above all titanium tetrachloride, are especially preferred.

The titanium compound (ii) in the liquid state may be one, or a mixture, of titanium compounds which are liquid themselves, or may be a solution of the titanium compound in a solvent such as hydrocarbons.

In the present invention, the solid titanium catalyst component (A) containing magnesium, titanium, halogen and a compound selected from the group consisting of esters of polycarboxylic acids and esters of polyhydroxy compounds can be prepared in the following manner.

A liquid hydrocarbon solution of the magnesium compound (i) is contacted with the titanium compound (ii) in the liquid state to form a solid product. Or a liquid hydrocarbon solution of a mixture of the magnesium compound (i) and the titanium compound (ii) is first prepared, and then a solid product is formed from it. The reaction of forming the solid product is carried out in the presence of at least one electron donor (D) specified

hereinabove, and the product is contacted with the ester (E) selected from the group consisting of esters of polycarboxylic acids and esters of polyhydroxy compounds during the formation of the solid product [embodiment (a)] or after the formation of the solid product [embodiment (b)].

The electron donor (D) is selected from the group consisting of monocarboxylic acid esters, aliphatic carboxylic acids, carboxylic acid anhydrides, ketones, aliphatic ethers, aliphatic carbonates, alkoxy group-containing alcohols, aryloxy group-containing alcohols, organic silicon compounds having an Si--O--C bond and organic phosphorus compounds having a P--O--C bond. Examples of preferred electron donors include C21 -C20 monocarboxylic acid esters, C1 -C20, preferably C1 to C6, aliphatic carboxylic acids, C4 -C20 carboxylic acid anhydrides, C3 -C20 ketones, C2 -C16 aliphatic ethers, C2 -C16 aliphatic carbonates, C3 -C20 alkoxy group-containing alcohols, C3 -C20 aryloxy group-containing alcohols, organic silicon compounds having an Si--O--C bond in which the organic group has 1 to 10 carbon atoms, and organic phosphorus compounds having a P--O--C bond in which the organic group has 1 to 10 carbon atoms.

Specific examples of the monocarboxylic acid esters are methyl formate, methyl acetate, ethyl acetate, vinyl acetate, propyl acetate, iso-butyl acetate, tertbutyl acetate, octyl acetate, cyclohexyl acetate, ethyl propionate, methyl butyrate, ethyl valerate, ethyl pyruvate, ethyl pivalate, methyl chloroacetate, ethyl dichloroacetate, methyl methacrylate, ethyl crotonate, methyl cyclohexanecarboxylate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, octyl benzoate, cyclohexyl benzoate, phenyl benzoate, benzyl benzoate, methyl toluate, ethyl toluate, amyl toluate, ethyl ethylbenzoate, methyl anisate, ethyl anisate, and ethyl ethoxybenzoate.

Specific examples of the aliphatic carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid and valeric acid.

Specific examples of the carboxylic acid anhydrides are acetic anhydride, maleic anhydride, benzoic anhydride, phthalic anhydride, trimellitic anhydride and tetrahydrophthalic anhydride.

Specific examples of the ketones are acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl n-butyl ketone, acetophenone, benzophenone, cyclohexanone, and benzoquinone.

Specific examples of the aliphatic ethers include methyl ether, ethyl ether, isopropyl ether, butyl ether, amyl ether, ethyl benzyl ether, ethylene glycol dibutyl ether, and anisole.

Specific examples of the alkoxy group-containing alcohols are butyl Cellosolve (ethylene glycol monobutyl ether) and ethyl Cellosolve (ethylene glycol monoethyl ether).

Specific examples of the aliphatic carbonates are dimethyl carbonate, diethyl carbonate, and ethylene carbonate.

Specific examples of the organic silicon compounds having as Si--O--C bond are methyl silicate, ethyl silicate and diphenyldimethoxysilane.

Specific examples of the organic phosphorus compounds having a P--O--C bond are trimethyl phosphite and triethyl phosphite.

If desired, these electron donor compounds may be formed in situ during the formation of the catalyst component (A).

Illustrative of preferred polycarboxylic acid esters or polyhydroxy compound esters used in the preparation of the catalyst component (A) are those having a skeleton represented by the formula wherein R@1 represents a substituted or unsubstituted hydrocarbon group; R@2, R@5 and R@6 represent a hydrogen atom or a substituted or unsubstituted hydrocarbon group; R@3 and R@4 represent a hydrogen atom or a substituted or unsubstituted hydrocarbon group and preferably at least one of R@3 and R@4 is a substituted or unsubstituted hydrocarbon group, or R@3 and R@4 may be linked to each

other; and the substituted hydrocarbon group mentioned above is a substituted hydrocarbon group containing a hetero atom such as N, O and S, for example one containing such a group as C--O--C, COOR, COOH, OH, SO₃ H, --C--N--C-- or NH₂.

Examples of the hydrocarbon group in the above formula include C₁ -C₁₀ alkyl groups such as a methyl, ethyl, propyl, butyl, amyl, hexyl or octyl group, C₆ -C₁₆ aryl groups such as a phenyl, tolyl, xylyl, benzyl or naphthyl group, C₁ -C₁₀ alkylidene groups such as a methylidene, ethylidene or propylidene group, and C₁ -C₁₀ alkenyl groups such as a vinyl, allyl or propenyl group. Examples of the ring formed by the bonding of R@3 and R@4 are cyclohexane, benzene, naphthalene, norbornane and cyclopentane rings.

These hydrocarbon groups may contain such substituents as exemplified above.

Among these electron donors (D), monocarboxylic acid esters, aliphatic carboxylic acids, carboxylic acid anhydrides, ketones, alkoxy group-containing alcohols and organic silicon compounds having an Si--O--C bond are preferred. The monocarboxylic acid esters and carboxylic acid anhydrides are especially preferred.

Specific examples of preferred polycarboxylic acid esters (E) include C₅ -C₃₀ aliphatic polycarboxylic acid esters such as diethyl methylsuccinate, diisobutyl alpha-methylglutarate, diethyl methylmalonate, diethyl ethylmalonate, diethyl isopropylmalonate, diethyl butylmalonate, diethyl phenylmalonate, diethyl diethylmalonate, diethyl dibutylmalonate, monoisooctyl maleate, diisooctyl maleate, diisobutyl maleate, diisobutyl butylmaleate, diisopropyl beta-methylglutarate, diallyl ethylsuccinate, di-2-ethylhexyl fumarate, diisooctyl citraconate, and esters of long-chain dicarboxylic acids (e.g., diethyl adipate, diisobutyl adipate, diisopropyl sebacate, di-n-butyl sebacate, di-n-octyl sebacate and di-2-ethylhexyl sebacate); C₁₀ -C₃₀ alicyclic polycarboxylic acid esters such as diethyl 1,2-cyclohexanecarboxylate and diisobutyl 1,2-cyclohexanecarboxylate; C₁₀ -C₃₀ aromatic polycarboxylic acid esters such as monoethyl phthalate, dimethyl phthalate, methylethyl phthalate, monoisobutyl phthalate, diethyl phthalate, ethyl isobutylphthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-heptyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, dineopentyl phthalate, didecyl phthalate, benzyl butyl phthalate, diphenyl phthalate, diethyl naphthalenedicarboxylate and dibutyl naphthalenedicarboxylate; and C₈ -C₃₀ heterocyclic polycarboxylic acid esters such as esters of 3,4-furandicarboxylic acid.

Illustrative of preferred esters of polyhydroxy compounds, (E), are esters formed between C₆ to C₁₆ aromatic polyhydroxy compounds and C₁ to C₁₂, preferably C₁ to C₇, aliphatic carboxylic acids such as 1,2-diacetoxybenzene, 1-methyl-2,3-diacetoxybenzene and 2,3-diacetoxynaphthalene.

In including the substance derived from the ester selected from the group consisting of esters of polycarboxylic acids and esters of polyhydroxy compounds into the catalyst component (A), it is not always necessary to use such a compound itself as a starting material. If desired, it is possible to use a compound capable of being converted to such a compound during the preparation of the titanium catalyst component (A) and convert it to the ester during the preparation of the catalyst component (A).

The amount of the electron donor (D) present during the formation of the solid product in the embodiment (a) or (b) is, for example, about 0.01 to about 1 mole, preferably about 0.05 to about 0.5 mole, per mole of the magnesium compound (i). By the selection of such an amount, the particle size of the solid product can be adjusted.

If the amount of the electron donor (D) is too large, it may be deposited too much on the solid product and may possibly exert adverse effects although the degree of adverse effects varies according to the type of the electron donor (D). It is preferred therefore to select a suitable amount within the above-exemplified range.

When the solid product is formed in the presence of the polycarboxylic acid ester and/or polyhydroxy compound ester, (E), in accordance with the embodiment (a), the ester (E) is used preferably in an amount of about 0.01 to about 1 mole, especially from about 0.1 to

about 0.5 mole, per mole of the magnesium compound (i). Preferably, the molar ratio of the ester (E) deposited on the solid product to the electron donor (D) is adjusted to 1: about 0.01-about 2, especially 1: about 0.1-about 1.

In order to form a solid product containing magnesium and titanium from a hydrocarbon solution of the magnesium compound (i) and the titanium compound (ii) in the liquid state, it is preferred to employ a method of reacting the two liquids by contacting them with each other. Preferably, a halogen-containing compound is used as the titanium compound (ii) in an amount sufficient to form the solid product. The amount of the titanium compound (ii) used may vary depending upon its type, the contacting conditions and the amounts of the electron donor (D) and other ingredients. Preferably, its amount is at least 1 mole, usually about 2 to about 200 moles, especially about 3 to about 100 moles, per mole of the magnesium compound (i).

If the solid product is difficult to form by the mere contacting of the liquid hydrocarbon solution of the magnesium compound (i) with the titanium compound (ii) in the liquid state, or if the solid product is difficult to form by simply leaving the hydrocarbon solution of the compounds (i) and (ii) to stand, an additional amount of the titanium compound (ii), preferably a halogen-containing titanium compound (ii), may be added, or another precipitating agent may be added, so as to form the solid product. Illustrative of such precipitating agent are halogenating agents such as halogens, halogenated hydrocarbons, halogen-containing silicon compounds, halogen-containing aluminum compounds, halogen-containing lithium compounds, halogen-containing sulfur compounds and halogen-containing antimony compounds. Specific examples are chlorine, bromine, hydrogen chloride, hydrochloric acid, phosphorus pentachloride, thionyl chloride, thionyl bromide, sulfonyl chloride, phosgene, and nitrosyl chloride.

The solid product differs in shape or size depending upon the conditions for its formation. In order to obtain a solid product having a uniform shape and a uniform particle size, it is preferred to avoid its rapid formation. For example, when the solid product is to be formed by mixing the compounds (i) and (ii) in the liquid state and reacting them with each other, it is advisable to mix them at a sufficiently low temperature which does not cause rapid formation of a solid product, and then to elevate the temperature gradually. According to this method, there can easily be obtained a granular or spherical solid product having a relatively large particle diameter and a narrow particle size distribution.

When slurry polymerization or vapor phase polymerization is carried out by using the granular or spherical solid catalyst component having a good particle size distribution which can be obtained as above, the resulting polymer is granular or spherical and has a narrow particle size distribution, a high bulk density and good flowability. The term "granular", as used herein denotes particles which look like an assembly of fine powders when examined by an enlarged scale photograph. Particles ranging from those having many uneven parts to those close to a true sphere can be obtained as the granular product depending upon the method of preparing the solid catalyst component.

The contacting of the liquid hydrocarbon solution of the magnesium compound (i) with the titanium compound (ii) in the liquid state may be effected, for example, at a temperature of about -70 DEG C. to about +200 DEG C. The temperatures of the two liquids to be contacted may be different from each other. Generally, it is frequently preferred to employ a contacting method not involving too high a temperature, in order to obtain a solid catalyst component having a desirable granular or spherical shape and high performance. For example, temperatures of about -70 DEG to about +50 DEG C. are preferred. If the contacting temperature is too low, precipitation of a solid product may sometimes be not observed. In such a case, it is desirable to elevate the temperature to about 50 DEG to about 150 DEG C. for example, or continue the contacting for a longer period of time until precipitation of the solid product occurs.

The solid product is preferably washed with an excess of a liquid titanium compound or a liquid halogenated hydrocarbon, preferably titanium tetrachloride, 1,2-dichloroethane, chlorobenzene, methyl chloride and hexachloroethane at least once at a temperature of, for example, about 20 DEG to about 150 DEG C. Then, the product is usually washed with a hydrocarbon and can be used in polymerization. Examples of the hydrocarbon may be the

same as those exemplified hereinabove with regard to the formation of the liquid hydrocarbon solution of the magnesium compound (i).

The method according to the embodiment (a) is excellent because its operation is simple and a solid catalyst component (A) of high performance can be obtained.

In the embodiment (b), the following procedure can be taken.

A suspension of the solid product is prepared after forming a hydrocarbon solution of the magnesium compound (i) and the titanium compound (ii) or by contacting the magnesium compound (i) in the liquid state and the titanium compound in (ii) in the liquid state as in the embodiment (a). Generally, a method can be employed in which the polycarboxylic acid ester and/or polyhydroxy compound ester is added to this suspension, and reacted at a temperature of, for example, about 0 DEG to about 150 DEG C. The amount of the electron donor used is the same as in the embodiment (a). The resulting solid product can be washed at least once with a liquid titanium compound, preferably an excess of titanium tetrachloride, at a temperature of about 20 DEG to about 150 DEG C.

If desired, the embodiments (a) and (b) may be used together in the present invention.

In the formation of the solid product in this invention in the manner described above, a porous inorganic and/or organic solid compound may be present so that the solid product is deposited on the surface of the porous solid compound. In this case, it is possible to preliminarily contact the porous solid compound with the magnesium compound (i) in the liquid state, and then contact the porous solid compound holding the liquid magnesium compound with the liquid titanium compound (ii).

Illustrative of the porous solid compound are silica, alumina, polyolefins, and products obtained by treating these compounds with halogen-containing compounds such as chlorine, bromine, hydrogen chloride, 1,2-dichloroethane and chlorobenzene.

The solid titanium catalyst component (A) used in this invention may be one obtained by the aforesaid embodiment (a) or (b), with or without further washing with a titanium compound, a hydrocarbon, etc.

Preferably, the solid titanium catalyst component (A) which can be obtained by any of the above-described embodiments is used for polymerization after it is well washed with a hydrocarbon. The resulting solid titanium catalyst component (A) preferably has such a composition that the magnesium/titanium atomic ratio is, for example, from about 2 to about 100, preferably from about 4 to about 50, more preferably from about 5 to about 30, the halogen/titanium atomic ratio is, for example, from about 4 to about 100, preferably from about 5 to about 90, more preferably from about 8 to about 50, and the electron donor/titanium mole ratio is, for example, from about 0.01 to about 100, preferably from about 0.2 to about 10, more preferably from about 0.4 to about 6. As stated hereinabove, the shape of the catalyst component (A) is, in many cases, granular or nearly spherical. Usually, it has a specific surface area of, for example, at least about 10 m²/g, preferably about 100 to about 1000 m²/g.

The halogen in the solid titanium catalyst component (A) is chlorine, bromine, iodine, fluorine, or two or more of these, preferably chlorine. The electron donor included in the catalyst component (A) at least contains the ester (E) selected from esters of polycarboxylic acids and esters of polyhydroxy compounds, and sometimes contains the electron donor (D) as well.

The ratio of the ester (E) to the other electron donor (D) varies depending upon the type of the electron donor (D). The catalyst component (A) shows good performance even if it contains not more than about 2 moles, preferably not more than about 1 mole, especially preferably not more than 0.5 mole, per mole of the ester (E).

According to this invention, olefins are polymerized by using a catalyst system composed of the solid titanium catalyst component (A) prepared as above, the organometallic compound (B) of the metal of Groups I to III of the periodic table, and the organic silicon

compound (C).

As examples of the organometallic compound (B), the following compounds may be cited.

(1) Organoaluminum compounds having at least one Al--C bond in the molecule, for example organoaluminum compounds of the general formula
 $R@1m Al(OR@2)n Hp Xq$

wherein R@1 and R@2 are identical or different and each represents a hydrocarbon group, for example a hydrocarbon group having 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, X represents a halogen atom, m is a number represented by 0

(2) Complex alkylated products of aluminum and a Group I metal represented by the general formula

$<\#s> M@1 AlR@14$

wherein M@1 represents Li, Na and K, and R@1 is as defined above.

(3) Dialkyl compounds of a Group III metal represented by the general formula
 $R@1 R@2 M@2$

wherein R@1 and R@2 are as defined above, and M@2 is Mg, Zn and Cd.

In the above formulae, examples of the hydrocarbon group for R@1 and R@2 are alkyl groups and aryl groups.

Examples of the organoaluminum compounds (1) are shown below.

Compounds of the general formula $R@1m Al(OR@2)3-m$ (wherein R@1 and R@2 are as defined above, m is preferably a number represented by 1.5.ltoreq.m.ltoreq.3:

compounds of the general formula $R@1m AlX3-m$ wherein R@1 is as defined above, X is halogen, and m is preferably a number represented by 0

compounds represented by the general formula $R@1m AlH3-m$ wherein R@1 is as defined above, and m is preferably a number represented by 2.ltoreq.m<3, and

$<\#s>$ compounds represented by the general formula $R@1m Al(OR@2)n Xq$ wherein R@1 and R@2 are as defined above, X represents halogen, 0

$<\#s>$ Specific examples of the organoaluminum compounds of formula (1) are trialkyl aluminums such as triethyl aluminum and tributyl aluminum; trialkenyl aluminums such as triisoprenyl aluminum; partially alkoxylated alkyl aluminums, for example, dialkyl aluminum alkoxides such as diethyl aluminum ethoxide and dibutyl aluminum butoxide; alkyl aluminum sesquialkoxides such as ethyl aluminum sesquiethoxide and butyl aluminum sesquibutoxide; compounds having an average composition expressed by $R@12.5 Al(OR@2)0.5$; partially halogenated alkyl aluminums, for example, dialkyl aluminum halide such as diethyl aluminum chloride, dibutyl aluminum chloride and diethyl aluminum bromide; alkyl aluminum sesquihalides such as ethyl aluminum sesquichloride, butyl aluminum sesquichloride and ethyl aluminum sesquibromide; alkyl aluminum dihalides such as ethyl aluminum dichloride, propyl aluminum dichloride and butyl aluminum dibromide; partially hydrogenated alkyl aluminums, for example, dialkyl aluminum hydrides such as diethyl aluminum hydride and dibutyl aluminum hydride, alkyl aluminum dihydrides such as ethyl aluminum dihydride and propyl aluminum dihydride; and partially alcoholated and halogenated alkyl aluminums, for example, alkyl aluminum alkoxyhalides such as ethyl aluminum ethoxychloride, butyl aluminum butoxychloride and ethyl aluminum ethoxybromide.

Examples of the compounds mentioned in (2) above are $LiAl(C_2H_5)_4$ and $LiAl(C_7H_{15})_4$.

Examples of the compounds mentioned in (3) above are diethyl zinc and diethyl magnesium. Alkyl magnesium halides such as ethyl magnesium chloride may also be used.

Organoaluminum compounds in which two or more aluminum atoms are bonded through an oxygen or nitrogen atom, similar to the compounds (1), may also be used. Examples of

such aluminum compounds are $(C_2H_5)_2AlOAl(C_2H_5)_2$.

Among the above organoaluminum compounds, trialkyl aluminums and alkyl aluminums in which two or more aluminums are bonded are preferred.

Illustrative of the organic silicon compound (C) having an $Si-O-C$ or $Si-N-C$ bond are alkoxysilanes and aryloxysilanes. For example, there may be cited organic silicon compounds represented by the following general formula



wherein R represents a hydrocarbon group, such as an alkyl, cycloalkyl, aryl, alkenyl, haloalkyl, or aminoalkyl group, or halogen. R@1 represents a hydrocarbon group such as an alkyl, cycloalkyl, aryl, alkenyl or alkoxyalkyl group, and n is a number represented by $0 \leq n \leq 4$, preferably $0 \leq n \leq 3$, and n R groups, or (4-n)OR@1 groups may be identical or different.

In the above formula, R is preferably a C_1-C_{20} hydrocarbon group, such as a C_1-C_{10} alkyl group, a C_5-C_{12} cycloalkyl group, a C_6-C_{20} aryl group, a C_1-C_{10} alkenyl group, a C_1-C_{10} haloalkyl group, or a C_1-C_{10} aminoalkyl group, and a halogen atom such as chlorine atom; and R@1 is preferably a C_1-C_{20} hydrocarbon group, such as a C_1-C_{10} alkyl group, a C_5-C_{12} cycloalkyl group, a C_6-C_{20} aryl group, a C_2-C_{10} alkenyl group, or a C_2-C_{10} alkoxy alkyl group.

Other examples of the catalyst component (C) include siloxanes having the group OR@1 and silyl esters of carboxylic acid. Examples of R@1 are the same as those exemplified above. There may also be used the product of reaction of a compound having no $Si-O-C$ bond with a compound having an $O-C$ bond obtained either in advance or in situ. For example, there can be cited the joint use of a halogen-containing silane compound containing no $Si-O-C$ bond or silicon hydride with an alkoxy group-containing aluminum compound, an alkoxy group-containing magnesium compound, another metal alcoholate, an alcohol, a formate ester, ethylene oxide, etc. The organic silicon compound may contain another metal such as aluminum and tin.

Examples of preferred organic silicon compounds as component (C) include trimethylmethoxysilane, trimethylethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diphenyldimethoxysilane, methylphenyldimethoxysilane, diphenyldiethoxysilane, ethyltrimethoxysilane, methyltrimethoxysilane, vinyltrimethoxysilane, phenyltrimethoxysilane, gamma-chloropropyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, butyltriethoxysilane, phenyltriethoxysilane, gamma-aminopropyltriethoxysilane, chlorotriethoxysilane, ethyltriisopropoxysilane, vinyltributoxysilane, ethyl silicate, butyl silicate, trimethylphenoxysilane, methyltriallyloxysilane, vinyltris(betamethoxyethoxy)silane, vinyltriacetoxysilane, dimethyltetraethoxydisiloxane and phenyldiethoxydiethylaminosilane. Of these, methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, vinyltriethoxysilane, phenyltriethoxysilane, vinyltributoxysilane, ethyl silicate, diphenyldimethoxysilane, diphenyldiethoxysilane and methylphenylmethoxysilane (the compounds of formula $R_n Si(OR@1)_{4-n}$ given above) are especially preferred.

The component (C) may be used in the form of an adduct with other compounds.

According to this invention, there is provided a process for producing olefin polymers or copolymers which comprises polymerizing or copolymerizing olefins or copolymerizing at least one olefin with a minor amount, for example up to 10 mole %, of a diene in the presence of a catalyst system composed of the solid titanium catalyst component (A), the organometallic compound (B) and the organic silicon compound (C).

Illustrative of olefins which can be used are olefins having 2 to 10 carbon atoms such as ethylene, propylene, 1-butene, 4-methyl-1-pentene and 1-octene. They may be homopolymerized or random-copolymerized or block-copolymerized. The diene may be a polyunsaturated compound such as conjugated dienes or nonconjugated dienes. Specific examples include butadiene, isoprene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, ethylidene norbornene, vinyl norbornene and 1,7-octadiene.

The catalyst system of this invention can be advantageously used in the polymerization of copolymerization of alpha-olefins having at least 3 carbon atoms, specifically in the polymerization or copolymerization of alpha-olefins having 3 to 10 carbon atoms or the copolymerization of at least one such alpha-olefin with up to 10 mole % of ethylene and/or a diene.

The catalyst system of this invention shows the excellent characteristic that when used in the polymerization of ethylene, it gives a high yield of a polymer having a narrow particle size distribution, a high bulk density and a narrow distribution of molecular weight.

The polymerization can be carried out either in the liquid or vapor phase. When the liquid-phase polymerization is carried out, inert solvents such as hexane, heptane and kerosene may be used as a reaction medium. If desired, the olefin itself may be used as the reaction medium. The amount of the catalyst can be properly selected. For example, in a preferred embodiment, per liter of the reaction solvent in the case of the liquid-phase reaction or per liter of the volume of the reaction zone in the case of the vapor-phase reaction, the component (A) is used in an amount of 0.0001 to 1 millimole as the titanium atom; the component (B) is used in such a proportion that the amount of the metal atom in the component (B) is 1 to 2,000 moles, preferably 5 to 500 moles, per mole of the titanium atom in the component (A); and the component (C) is used in such a proportion that the amount of the silicon atom in the component (C) is 0.001 to 10 moles, preferably 0.01 to 2 moles, especially preferably 0.05 to 1 mole, per mole of the metal atom in the component (B).

The catalyst components (A), (B) and (C) may be contacted with one another before or during the polymerization. In contacting them before the polymerization, only two of them may be freely selected and contacted. Or two or three components may be partly taken up and contacted with each other. The contacting of these components before the polymerization may be carried out in an atmosphere of an inert gas or in an atmosphere of an olefin.

The polymerization temperature is preferably about 20 DEG to about 200 DEG C., more preferably about 50 DEG to about 180 DEG C. The pressure is from atmospheric pressure to about 100 kg/cm², preferably from about 2 to about 50 kg/cm². The polymerization can be carried out batchwise, semicontinuously, or continuously. Or the polymerization may also be carried out in two or more stages having different reaction conditions.

When the process of this invention is applied to the stereospecific polymerization of alpha-olefins having at least 3 carbon atoms, polymers having a high stereospecificity index can be produced with a high catalytic efficiency. While an attempt to obtain a polymer having a high melt index by using hydrogen in the polymerization of an olefin using the hitherto proposed solid titanium-containing catalyst components tends to result in not a small reduction in stereospecificity, the use of the catalyst system in accordance with this invention can reduce this tendency.

Having regard to the high activity of the catalyst, the yield of the polymer per unit amount of the solid titanium catalyst component (A) is larger than that in the prior art when polymers of the same stereospecificity index are to be obtained. Hence, the catalyst residue, particularly the halogen content, of the resulting polymer can be decreased. This not only enables the catalyst removing operation to be omitted, but also can markedly inhibit the corroding tendency of molds during molding.

When the process of this invention is applied to slurry polymerization or vapor phase polymerization, there can be formed a granular or nearly spherical polymer which looks as if it were the product of aggregation of fine powders. Such a granular or spherical polymer has good flowability and in some applications, can be directly used without pelletization. Another advantage is that the melt index of the polymer can be changed by using a lesser amount of a molecular weight controlling agent such as hydrogen than in the case of conventional catalyst systems, and that surprisingly, by increasing the amount of the molecular weight controlling agent, the activity of the catalyst rather tends to increase contrary to the conventional catalysts. With the conventional catalyst systems, the

increasing of the amount of the molecular weight controlling agent in an attempt to obtain a polymer having a high melt index leads to the decrease of the partial pressure of the olefin monomer and naturally to the decrease of the activity of the catalyst system. The catalyst system of this invention gives rise to no such problem, and its activity is rather increased by increasing the amount of the molecular weight controlling agent.

While the conventional catalyst systems decrease in activity with the passage of the polymerization time, such a phenomenon is scarcely noted in the catalyst system of this invention. The present invention brings about the advantage that even when the catalyst system is used in a multi-stage continuous polymerization process, the amount of the polymer product can be greatly increased.

Since the catalyst system of this invention is very stable at high temperatures, a reduction in stereospecificity is hardly observed even when propylene is polymerized at a temperature of, for example, about 90 DEG C.

The following Examples illustrate the present invention more specifically.

EXAMPLE 1

Preparation of a solid titanium catalyst component (A)

Anhydrous magnesium chloride (4.76 g; 50 millimoles), 25 ml of decane and 23.4 ml (150 millimoles) of 2-ethylhexyl alcohol were reacted at 130 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution, and the mixture was further stirred at 130 DEG C. for 1 hour to dissolve phthalic anhydride in the uniform solution. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 200 ml (1.8 moles) of titanium tetrachloride kept at -20 DEG C. After the addition, the mixture was heated to 110 DEG C. over the course of 4 hours, and when a temperature of 110 DEG C. was reached, 2.68 ml (12.5 millimoles) of diisobutyl phthalate was added. The mixture was then maintained at this temperature for 2 hours with stirring. After the reaction, the reaction mixture was hot-filtered to collect the solid portion. The solid portion was again suspended in 200 ml of titanium tetrachloride, and reacted at 110 DEG C. for 2 hours. After the reaction, the solid portion was collected by hot filtration and washed with decane kept at 110 DEG C. and hexane until no free titanium compound was detected in the washings.

The solid titanium catalyst component (A) synthesized by the above method was stored as a slurry in hexane. A part of the slurry was dried in order to examine the composition of the catalyst. It was found that the resultant solid titanium catalyst component (A) contained 3.1% by weight of titanium, 56.0% by weight of chlorine, 17.0% by weight of magnesium and 20.9% by weight of diisobutyl phthalate.

Polymerization

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.125 millimole of phenyltriethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) prepared as above were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm²G.

After the polymerization, the slurry containing the resulting polymer was filtered to separate it into a white powdery polymer and a liquid layer. After drying, the amount of the white powdery polymer was 379.2 g. The polymer had a boiling n-heptane extraction residue of 98.9%, a melt index (MI) of 7.5 and an apparent density of 0.44 g/ml. The particle size distribution of the white powdery polymer was as shown in Table 1. Concentrating the liquid layer yielded 1.9 g of a solvent-soluble polymer. Accordingly, the activity was 25,400 g-PP/mole-Ti, and the isotacticity index (II) of the entire polymer was 98.4%.

TABLE 1

> > 1190.mu.840.mu.>420.mu.>250.mu.>177.mu.>105.mu.>44.mu.44.mu>

0 0 4.1 95.7 0.2 0 0 0

EXAMPLES 2 TO 6

Example 1 was followed except that the amount of hydrogen used in the polymerization was changed to 100 ml, 400 mml, 800 ml, 1,000 ml and 2,000 ml, respectively. The results are shown in Table 2.

TABLE 2

Example	Amount of hydrogen (ml)	MI	Activity (g-PP/mmol-Ti)	II(%) of the white powdery polymer	II (%) of the entire polymer
2	100	2.7	20,000	98.9	98.4
1	200	7.5	25,400	98.9	98.4
3	400	20	30,800	98.6	98.0
4	800	69	32,100	98.3	97.7
5	1000	145	34,000	97.7	97.0
6	2000	280	29,600	97.4	96.6

EXAMPLES 7 AND 8

Example 1 was followed except that the polymerization temperature was changed to 80 DEG C. and 90 DEG C., respectively. The results are shown in Table 3.

TABLE 3

Example	Polymerization temperature (DEG C.)	Activity (g-PP/mmole-Ti)	II (%) of the white powdery polymer	II (%) of the entire polymer	Bulk density	MI
1	70	25,400	98.9		98.4	
0.44 7.4						
7	80	25,300	99.2		98.6	
0.43 10.1						
8	90	22,600	98.7		98.1	
0.41 21.3						

EXAMPLE 9

A 2-liter autoclave was charged with 500 g of propylene, and at room temperature, 0.25 mmole of triethyl aluminum, 0.025 millimole of diphenyldimethoxysilane and 0.005 mmole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. Hydrogen (750 ml) was further introduced into the autoclave. The temperature was raised to 80 DEG C., and propylene was polymerized for 1 hour. After drying, the amount of the entire polymer yielded was 192.3 g. The entire polymer had a boiling n-heptane extraction residue of 98.6%, an MI of 3.2 and an apparent density of 0.48 g/ml. Hence, the activity at this time was 38,500 g-PP/mmole-Ti.

EXAMPLES 10 TO 14

Example 9 was followed except that 0.375 millimole of triethyl aluminum, 0.0188 millimole of phenyltriethoxysilane and 0.0025 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were used in the polymerization, and the polymerization time was changed to 15 minutes, 30 minutes, 1 hour, 2 hours, and 3 hours.

respectively. The results are shown in Table 4.
TABLE 4

Example	Polymerization time (minutes)	Activity (g-PP/mole-Ti)	II (%) of the entire polymer	Bulk density (g/ml)
10	15	10.400	97.0	0.47
11	30	25.200	98.2	0.48
12	60	32.800	98.3	0.49
13	120	72.400	97.9	0.48
14	180	88.400	97.9	0.49

EXAMPLE 15

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.125 millimole of diphenyldimethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm²G. The reaction mixture was worked up by the same procedure as in Example 1. The results are shown in Table 5.

EXAMPLE 16

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.225 millimole of phenyltrimethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 was charged. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm²G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 17

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.30 millimole of vinyltrimethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 4 hours. During the polymerization, the pressure was maintained at 7 kg/cm²G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 18

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.45 millimole of methyltrimethoxysilane and 0.015 millimoles, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm²G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 19

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.30 millimole of tetraethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst

component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 4 hours. During the polymerization, the pressure was maintained at 7 kg/cm@2.G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 20

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.225 millimole of ethyltriethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 4 hours. During the polymerization, the pressure was maintained at 7 kg/cm@2.G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 21

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.225 millimoles of vinyltriethoxysilane and 0.015 millimoles, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 4 hours. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 22

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 2.51 millimoles of triethyl aluminum, 0.225 millimole of methylphenyldimethoxysilane and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm@2.G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

EXAMPLE 23

A 2-liter autoclave was charged with 750 ml of purified hexane, and in an atmosphere of propylene at room temperature, 1.8 millimoles of triethyl aluminum, 0.45 millimole of monochlorodiethyl aluminum, 0.12 millimole of phenyltriethoxysilane, and 0.015 millimole, calculated as the titanium atom, of the catalyst component (A) described in Example 1 were introduced into the autoclave. After introducing 200 ml of hydrogen, the temperature was raised to 70 DEG C., and propylene was polymerized for 2 hours. During the polymerization, the pressure was maintained at 7 kg/cm@2.G. The reaction mixture was worked up in the same way as in Example 1. The results are shown in Table 5.

TABLE 5

Example	Organic silicon compound(C)	Activity	II (%) of the	MI	Bulk
			(g-PP/mole-Ti)	entire polymer	
					density
15	Diphenyldimethoxysilane	31,600	98.9	6.3	0.45
16	Phenyltrimethoxysilane	23,700	98.6	5.2	
0.45					
17	Vinyltrimethoxysilane	19,200	97.6	25.0	
0.44					
18	Methyltrimethoxysilane	23,300	96.9	11.4	
0.44					

0.43	19	Tetraethoxysilane	22.300	96.8	58.0
0.44	20	Ethyltriethoxysilane	22.200	98.0	24.0
0.43	21	Vinyltriethoxysilane	18.700	98.0	27.0
0.45	22	Methylphenyldimethoxysilane	29.700	98.6	4.2
0.44	23	Phenyltriethoxysilane	23.100	97.6	7.6

EXAMPLE 24

Preparation of a solid titanium catalyst component (A)

Anhydrous magnesium chloride (4.76 g; 50 millimoles), 25 ml of decane and 23.4 ml (150 millimoles) of 2-ethylhexyl alcohol were reacted at 130 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution. The mixture was stirred at 130 DEG C. for 1 hour to dissolve phthalic anhydride. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 200 ml (1.8 moles) of titanium tetrachloride kept at -20 DEG C. After the addition, the temperature of the mixed solution was raised to 110 DEG C. over the course of 4 hours. When the temperature reached 110 DEG C., 3.5 g (12.5 millimoles) of di-n-butyl phthalate was added, and the mixture was maintained at the same temperature for 2 hours. After the lapse of the two hours, the solid portion was collected by hot-filtration from the reaction mixture. The solid portion was again suspended in 200 ml of titanium tetrachloride, and again heated at 120 DEG C. for 2 hours. After the reaction, the solid portion was collected by hot filtration, and washed fully with decane kept at 120 DEG C. and hexane until no free titanium compound was detected in the washings.

The resulting catalyst component (A) was stored as a slurry in hexane. A part of the slurry was dried in order to examine the composition of the catalyst. The resulting catalyst component (A) was found to contain 2.1% by weight of titanium.

Propylene was polymerized by using the resulting solid titanium catalyst component in the same way as in Example 1. The results are shown in Table 6.

EXAMPLE 25

Preparation of a solid titanium catalyst component (A)

Anhydrous magnesium chloride (4.76 g; 50 millimoles), 25 ml of decane and 23.4 ml (150 millimoles) of 2-ethylhexyl alcohol were reacted at 130 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution, and the mixture was stirred at 130 DEG C. for 1 hour to dissolve phthalic anhydride. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 200 ml (1.8 moles) of titanium tetrachloride kept at -20 DEG C. After the addition, the mixture was heated to 110 DEG C. over the course of 4 hours. When the temperature reached 110 DEG C., 2.6 ml (13.0 millimoles) of diethyl phthalate was added. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture by hot filtration. The solid portion was again suspended in 200 ml of titanium tetrachloride and again reacted at 120 DEG C. for 2 hours. After the reaction, the solid portion was again collected by hot filtration, and washed with decane at kept at 120 DEG C. and hexane until no free titanium compound was detected in the washings.

The resulting solid titanium catalyst component (A) prepared as above was stored as a slurry in hexane. A part of the slurry was dried in order to examine the composition of the catalyst. The resulting solid titanium catalyst component (A) was found to contain 4.0% by weight of titanium.

Using the resulting solid titanium catalyst component (A), propylene was polymerized in the same way as in Example 1. The results are shown in Table 6.

EXAMPLE 26

Preparation of a solid titanium catalyst component (A)

Anhydrous magnesium chloride (4.76 g; 50 millimoles), 25 ml of decane and 23.4 ml (150 millimoles) of 2-ethylhexyl alcohol were reacted at 130 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution, and the mixture was stirred at 130 DEG C. for 1 hour to dissolve the phthalic anhydride. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 200 ml (1.8 moles) of titanium tetrachloride kept at -20 DEG C. After the addition, the mixture was heated to 110 DEG C. over the course of 4 hours. When the temperature reached 110 DEG C., 2.9 ml (12.5 millimoles) of diisopropyl phthalate was added, and the mixture was maintained at the same temperature for 2 hours. After the reaction for two hours, the solid portion was collected from the reaction mixture by hot filtration. The solid portion was again suspended in 200 ml of titanium tetrachloride, and again reacted at 120 DEG C. for 2 hours. After the reaction, the solid portion was again collected by hot filtration, and washed with decane kept at 120 DEG C. and hexane until no free titanium compound was detected in the washings.

The solid titanium catalyst component (A) prepared as above was stored as a slurry in hexane. A part of the slurry was dried in order to examine the composition of the catalyst. The resulting solid titanium catalyst component (A) was found to contain 2.9% by weight of titanium.

Using the resulting solid titanium catalyst component (A), propylene was polymerized in the same way as in Example 1. The results are shown in Table 6.

TABLE 6

density	Example	Ester (E)	Activity (g-PP/mmole-Ti)	II (%) of the entire polymer	MI Bulk
0.42	24	Di-n-butylphthalate	23.000	97.6	2.9
0.44	25	Diethyl phthalate	18.300	97.5	11.1
0.44	26	Diisopropyl phthalate	20.100	97.3	9.2

EXAMPLE 27

Preparation of a catalyst component (A)

C2.H5 OMgCl (5.25 g), 23.2 ml of 2-ethylhexyl alcohol and 50 ml of decane were mixed at room temperature for about 1 hour. To the resulting uniform solution was added 1.11 g of phthalic anhydride, and the reaction was carried out at 130 DEG C. for 1 hour to dissolve phthalic anhydride in the uniform solution. The solution was then cooled to room temperature. The uniform solution thus obtained was added dropwise with stirring over 1 hour to 200 ml of titanium tetrachloride kept at -20 DEG C. The mixture was worked up in the same way as in Example 1 to form a catalyst component (A).

Polymerization

Propylene was polymerized in the same way as in Example 15 except that the catalyst component (A) prepared as above was used. The polymerization activity was 23.700 g-PP/mmole-Ti, and the entire polymer had an II of 96.0%. The apparent density of the polymer was 0.42 g/ml.

EXAMPLE 28

Preparation of a catalyst component (A)

A decane solution (150 ml) containing 50 millimoles of ethyl butyl magnesium and 17.0 ml of 2-ethylhexanol were reacted at 80 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution to form a fully uniform solution. The uniform solution was added dropwise with stirring over the course of 1 hour to 200 ml of titanium tetrachloride kept at -20 DEG C. Then, the same operation as in Example 1 was performed to give the catalyst component (A).

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting catalyst component (A). The results are shown in Table 7.

EXAMPLE 29

Preparation of a catalyst component (A)

Anhydrous magnesium chloride (4.76 g; 50 millimoles), 25 ml of decane, 3.4 ml (10 millimoles) of tetrabutoxytitanium and 17.9 ml (115 millimoles) of 2-ethylhexyl alcohol were reacted at 130 DEG C. for 2 hours to form a uniform solution. Phthalic anhydride (1.11 g; 7.5 millimoles) was added to the solution, and the mixture was stirred at 130 DEG C. for 1 hour to dissolve phthalic anhydride. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 200 ml (1.8 moles) of titanium tetrachloride kept at -20 DEG C. Then, the same operation as in Example 1 was performed to give the solid titanium catalyst component (A).

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid titanium catalyst component (A). The results are shown in Table 7.

TABLE 7

Example	Activity (g-PP/mole-Ti)	II (%) of the entire polymer	MI	Bulk density
28	23,200	97.6	8.1	0.43
29	24,300	98.1	3.5	0.43

EXAMPLE 30

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 1.43 ml (10 millimoles) of ethyl benzoate was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The catalyst component (A) contained 2.4% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 1 using the resulting solid catalyst component (A). The results are shown in Table 8.

EXAMPLE 31

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was synthesized in the same way as in Example 1 except

that 1.80 ml (15.6 millimoles) of benzoyl chloride was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride and 2-ethylhexyl benzoate was formed during the preparation of the catalyst. The resulting solid catalyst component (A) contained 3.1% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 1 using the resulting solid catalyst component (A). The results are shown in Table 8.

EXAMPLE 32

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 1.47 ml (15 millimoles) of methyl acetate was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 4.7% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid titanium catalyst component (A). The results are shown in Table 8.

EXAMPLE 33

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (a) was prepared in the same way as in Example 1 except that 1.12 ml (15 millimoles) of propionic acid was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 3.1% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the solid catalyst component (A). The results are shown in Table 8.

EXAMPLE 34

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 1.46 ml (7.5 millimoles) of diphenyl ketone was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 2.5% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid titanium catalyst component (A). The results are shown in Table 8.

EXAMPLE 35

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was synthesized in the same way as in Example 1 except that 1.82 ml (15 millimoles) of diethyl carbonate was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 4.3% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid catalyst component (A). The results are shown in Table 8.

EXAMPLE 36

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 0.88 ml (7.5 millimoles) of tetramethyl silicate was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 5.1% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid titanium catalyst component (A). The results are shown in Table 8.

EXAMPLE 37

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 0.99 ml (7.5 millimoles) of n-butyl Cellosolve was used instead of 1.11 g (7.5 millimoles) of phthalic anhydride. The resulting solid catalyst component (A) contained 5.5% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting solid catalyst component (A). The results are shown in Table 8.

EXAMPLE 38

Preparation of a solid titanium catalyst component (A)

A solid catalyst component (A) was prepared in the same way as in Example 1 except that 4.86 ml (20 millimoles) of 2-ethylhexyl benzoate was used instead of 1.1 g (7.5 millimoles) of phthalic anhydride. The resulting catalyst component (A) contained 3.1% by weight of titanium.

Polymerization

Propylene was polymerized in the same way as in Example 15 using the resulting titanium catalyst component (A). The results are shown in Table 8.

TABLE 8

Exa- mple	Activity II (%) (g-PP/ mmole-Ti)	MI Bulk density	Particle size distribution (wt %)									
			>1190.mu.	>840.mu.	>420.mu.	>250.mu.	>177.mu.	>105.mu.	>44.mu.	44.mu.	>	
0.3	30	23.200	97.6	8.1	0.43	0	0	0	4.7	56.8	38.2	
	31	25.400	97.4	4.1	0.40	0	0	0	5.0	79.4	15.2	
0.4	32	17.700	97.8	2.4	0.35	0	0	0.4	94.8	3.8	1.0	0
0	33	25.100	97.3	3.1	0.43	0	0	0	0.3	4.4	59.7	
35.6	34	31.100	97.3	3.2	0.37	0	0	0	10.2	48.1	41.3	
0.4	35	16.300	98.1	1.9	0.37	0	0.2	0.8	8.9	81.3	8.6	

[illegible]